ONTARIO MINISTRY OF THE ENVIRONMENT TORONTO, ONTARIO

DEVELOPMENT OF SEDIMENT QUALITY
OBJECTIVES
PHASE I - OPTIONS

Final Report

Prepared by:

BEAK CONSULTANTS LIMITED 6870 Goreway Drive Mississauga, Ontario L4V 1P1

October 1987 2369,1

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EXECUTIVE SUMMARY

A literature and database review study was undertaken as a basis for the identification of the strategies or options to be used for the development of numerical contaminant-specific sediment quality objectives. The study included review and synthesis of existing literature on biological effects of sediment contaminants (Workplan A), analysis of MOE In-Place Pollutants Program data to determine the extent to which contaminant body burdens of benthic organisms were related to sediment chemical characteristics (Workplan B), and review of alternative approaches to development of sediment quality objectives, the data requirements of each approach and data availability (Workplan C). A strategy for combined application of the various approaches to arrive at a numerical criterion was proposed.

Nine different approaches were described, including approaches based on sediment 'background' concentrations, sediment-water-biota partitioning coefficients applied to existing water or tissue objectives, concentration-biological response relationships from field studies, and concentration-response relationships from laboratory (single contaminant) studies. MOE In-Place Pollutants Program data may help to develop appropriate partitioning coefficients or concentration-response relationships, particularly for persistent organic contaminants which show the strongest partitioning relationships. Chemical partitioning and biological response data are currently lacking for some contaminants. Sediment background data are available for most contaminants addressed in this study.

A need to explicitly define the intent of sediment quality objectives was identified as an essential first step in criterion development, since value judgements of this nature determine the choice of appropriate coefficients and other input data which will be utilized in deriving criteria. An explicit statement of intent amounts to a toxicity objective which should be endorsed by the regulatory agency prior to criterion development.

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1.0 INTRODUCTION

Sediments are the principal reservoir or sink for persistent toxic chemicals in aquatic systems. An increasing emphasis on studies of the distribution, geochemistry and biological effects of persistent toxic substances in sediments of the Great Lakes basin has occurred since 1970, when mercury contamination of sediments and fish in Lake St. Clair was publicized and became a matter of disquiet at both public and governmental levels. Subsequently, the association between persistent toxic substances and sediment has been well documented.

In the early 1970's, the Ontario Water Resources Commission (OWRC) developed guidelines for evaluating dredge spoils for open-water disposal (Persaud and Wilkins, 1976). The parameter levels selected by the OWRC were modified from U.S. criteria and reflected results of studies undertaken in Canadian harbours on the Great Lakes. The guidelines were based on data that indicated an association of certain elevated levels of contaminants with impaired water quality and/or the absence of certain benthic indicator species. In the case of mercury, the guideline was based on an apparent correlation with mercury levels in fish higher than the 0.5 ppm guideline for human consumption. Overall, however, the individual parameter levels were empirically derived and relate more to some incremental change above background levels for the nearshore zone of the Great Lakes than to a level related to known adverse effects on biota. These guidelines have also been used to evaluate sediment quality during routine surveillance and monitoring studies.

Guidelines were developed for 11 heavy metals, nutrients, PCB's, cyanide and oil and grease (Table 1.1). The guidelines are based on bulk chemical analysis and, therefore, relate to the 'total' concentration of a respective chemical present in a given sediment sample. This approach provides basic guidance in environmental protection. However, it is not totally satisfactory for assessing the biological significance of contaminants in sediments, since the total concentrations of contaminants have generally little relationship to the amount released to the water column or their availability to biological organisms. Many studies have shown that a large fraction of heavy metals in sediments is not readily released to the water column or available for uptake by biota because it is associated with the mineral lattice of crystalline solids, strongly sorbed to particulate surfaces, or incorporated in organic materials (Gibbs, 1973; Walters and Wolery, 1974;

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TABLE 1.1: MOE GUIDELINES FOR OPEN-WATER DISPOSAL OF DREDGE $$\operatorname{\mathsf{SPOILS}}^1$$

	Guideline Concentration	
Parameter	(ug/g, unless otherwise indicated	
W.L.CL 6 P.L (0)	,	
Volatile Solids (%)	6	
COD (%)	5	
Total Kjeldahl Nitrogen	2,000	
Ammonia	100	
Total Phosphorus	1,000	
Oil and Grease	1,500	
Cyanide	0.1	
PCB's	0.05	
Arsenic	8.0	
Cadmium	1.0	
Chromium	25	
Cobalt	50	
Copper	25	
Iron	10,000	
Lead	50	
Mercury	0,3	
Nickel	25	
Silver	0.5	
Zinc	100	

¹ Persaud and Wilkins (1976).

Brannon et al., 1976a). Similarly, organic compounds, such as PCB's and organochlorine pesticides, generally have a low solubility and are tightly sorbed by clay particles and organic matter (Pionke and Chesters, 1973; Karickhoff et al., 1979).

In 1977, the United States Environmental Protection Agency (U.S. EPA)/United States Army Corps of Engineers (U.S. COE) Technical Committee on Criteria for Dredged and Fill Material developed a sediment bioassay implementation manual (U.S. EPA/U.S. COE, 1977). This manual provided the first formalized guidance for assessing the toxicological impact of dredged material disposal. It has become the standard reference for regulatory testing of dredged material prior to marine open water or confined disposal, and has been adopted by all U.S. Army COE Districts involved in ocean water disposal of dredged material. Basically, the procedures involve acute toxicity tests comparing the survival of sensitive aquatic organisms exposed to solid or liquid phases of candidate dredged material to the survival of those exposed to phases of uncontaminated reference sediments. Bioaccumulation potential is tested by analyzing tissues of surviving bioassay organisms after ten days exposure for elevated concentrations of contaminants. In the Great Lakes Basin, the U.S. Army COE Districts rely primarily on bulk chemical characterization of sediments and comparison with U.S. EPA (1977) guidelines for the pollutional classification of Great Lakes habour sediments. Elutriate and acute toxicity testing have been used less frequently, although Buffalo District has unilaterally embarked on a comprehensive program of acute toxicity testing of harbour and navigational waterway sediments using the mayfly nymph Hexagenia limbata, the waterflea Daphnia magna and the fathead minnow Pimephales promelas (Revin, 1987).

As part of the U.S. EPA/U.S. COE regulatory initiative, comprehensive research programs have been or are being undertaken to address the development of impact prediction and assessment methods for dredged spoil disposal. These include the U.S. COE Dredged Material Research Program (Saucier et al., 1978), the ongoing Long-term Effects of Dredging Operations Program (e.g., Dillon, 1984), the ongoing Dredging Operations Technical Support Program (e.g., Salamon, 1984), and other work associated with the Waterways Experiment Station at Vicksburg, Mississippi (e.g., Peddicord et al., 1986). Research work resulting from these initiatives included evaluations of bioassay testing (e.g., Shuba et al., 1977; Rosenberger et al., 1978), chemical release potential (e.g., Jones and Lee, 1978), and bioaccumulation potential (e.g., Neff et al., 1978; Dillon, 1984). These evaluations extended to the implementation and assessment of specific

protocols and methodologies during comprehensive field investigations in marine and Great Lakes locations (e.g., Sweeney, 1978; Salamon, 1984), as well as to the development of predictive models (e.g., McFarland, 1983).

Under the Great Lakes Water Quality Agreement of 1978, the Dredging Subcommittee of the Great Lakes Water Quality Board (GLWQB) of the International Joint Commission (IJC) is responsible for the delineation of "specific criteria for the classification of polluted sediments of designated areas of intensive and continuing dredging activities within the Great Lakes system" (IJC, 1978). The development of compatible guidelines and criteria for dredging activities has been ongoing (Dredging Subcommittee, 1982), and includes a two-harbour evaluation to assess the practicality of the guidelines (Dredging Subcommittee, 1983, 1986).

Environment Canada and Fisheries and Oceans Canada have supported literature reviews and evaluations of available bioassessment methods for contaminated sediments (BEAK, 1980; Craig, 1984; Munawar et al., 1984). The resulting reports were used primarily as background documents in attempting to gain concensus among Federal, Provincial and State agencies in adopting a common bioassessment approach to testing dredged sediments in the Great Lakes.

The MOE has supported a number of studies related to the assessment of dredging and dredged material disposal. For example, Krantzberg and Stokes (1983) developed a method for classifying the pollution status of sediments, involving physical (grain size) characterization, elutriate testing, fractionation and bioassay testing. BEAK/OCEANCHEM (1986) prepared a handbook of guidelines for dredging and dredged material disposal, which included recommended protocols for sediment bioassessment as well as tentative numerical sediment quality objectives for some persistent organic contaminants. Mudroch et al. (1986) have undertaken a review of the existing MOE guidelines for dredged material open water disposal based on a comprehensive review of the background and surficial concentrations of contaminants in sediments, including harbours, river mouths, bluffs and embayments of the Great Lakes. These initiatives have been jointly supported by Environment Canada.

The historic deposition of persistent toxic substances into sediments has been singled out by the IJC as a major concern in many localized areas around the Great Lakes (IJC, 1985). Contaminated sediments from past discharges resulting in in-place pollutants are identified as a problem in 38 of the 42 areas of concern in the Great Lakes and connecting channels (IJC, 1983). These sediments can be a source of pollutants into and through the food chain. The GLWQB has recommended that methods be developed to determine the site-specific significance of in-place pollutants to permit evaluation of the effectiveness of alternative approaches to remediation.

Consequently, the MOE recently initiated the In-Place Pollutants Program to assess the impacts of in-place pollutants in sediments on the aquatic ecosystem and human health (e.g., Lomas and Persaud, 1987; Persaud and Lomas, 1987). The resulting database provides site-specific information on contaminant concentrations in sediments (including distribution of metal levels among sediment fractions), in benthic invertebrates and in bottom-feeding fish (sculpin), as well as the distribution and abundance of benthic invertebrates for various areas of the Great Lakes (e.g., Jaagumagi, 1987; Persaud et al., 1987).

As a result of these and other initiatives, a large database has been developed on:

- o the release of contaminants in sediment to the overlying water;
- o the lethal and sublethal effects of contaminated sediments on benthic biota; and
- bioaccumulation of contaminants from sediments by benthic biota and the potential for food chain biomagnification.

This large and expanding database appears now to provide sufficient background information for the development of sediment quality objectives for specific contaminants or contaminant classes.

The Polluted Sediments Committee under the Canada-Ontario Agreement (COA) has retained Beak Consultants Limited (BEAK) to prepare a review and assessment of this database as a basis for the identification of the strategies or options to be used in sediment quality objectives development. The results of this study phase (Phase I) will be then used to derive specific numerical objectives (Phase II). The Phase II work, i.e., the actual development of the guidelines, will be carried out under separate contract. This undertaking is not merely an update of the existing MOE guidelines for dredged material

disposal in open water. The objectives to be developed are aimed at protecting aquatic life and water quality.

1.1 BEAK's Study Approach

The objective of this study was to develop the strategies or options to be used in deriving sediment quality objectives for the protection of aquatic life and water quality and uses in Ontario.

The study involved three major areas of investigation (workplans):

Workplan A

- literature and database search;
- o data tabulation:
- review and evaluation of data on sediment toxicity;
- o review and evaluation of data on bioaccumulation and biomagnification potential;
- o review and evaluation of data on chemical release potential; and
- o review and evaluation of data on benthic community structure effects.

Workplan B

review and statistical analysis of the MOE In-Place Pollutants Program.

Workplan C

o delineation of strategies or options for sediment quality objectives development.

A synopsis of BEAK's study approach to each of the three workplans is provided below.

In Workplan A, the literature search included journals, books, theses, abstracts, reports, progress reports, manuscripts and personal communications. The emphasis of the literature search was on research published or undertaken within the last ten years in relation to the influence of contaminated freshwater sediments (with particular emphasis on the Great Lakes) on:

- lethal and sublethal toxicity to benthic macroinvertebrates and bottomfeeding fish;
- bioaccumulation and biomagnification by benthic macroinvertebrates and bottom-feeding fish;
- o the release of contaminants to the water column; and
- o benthic macroinvertebrate species diversity and density.

The literature search and review was limited to the following toxic metals and organics:

- metals: arsenic, cadmium, chromium, copper, iron, lead, manganese, mercury, nickel and zinc.
- o PCB's, and
- pesticides: aldrin, α-BHC, β-BHC, γ-BHC, α-chlordane, γ-chlordane, oxychlordane, o,p-DDT, p,p-DDD, p,p-DDT, p,p-DDE, dieldrin, endrin, HCB, heptachlor, heptachlor epoxide and mirex.

However, studies identified during the literature search involving other toxic contaminants were listed. In addition, literature on the role of solvent extractables, organic matter and oxygen status of the sediment in relation to the health of the sediment ecosystem and contaminant availability was addressed.

The acquired articles, reports and databases were reviewed to abstract and tabulate data relevant to sediment toxicity, chemical release potential, bioaccumulation/biomagnification potential and benthic macroinvertebrate community structure. The data collected were entered into a comprehensively-designed spreadsheet database format for easy cross-referencing and data retrieval. In this way, toxicity, bioaccumulation, chemical release and other relevant data can be easily accessed by the Polluted Sediments Committee and subsequent contractors for the development of numerical sediment quality criteria. All data entered into the database were verified by BEAK staff not involved with the original data input.

The intent of the data tabulation was not to be all-inclusive in available data coverage. Instead, the intent was to provide an indication of the type and extent of data available for specific contaminants, and to identify the approaches most feasible and productive for sediment quality criteria development.

All available information regarding the influence of contaminated freshwater sediments (with particular emphasis on the Great Lakes) on toxicity (including genotoxicity) to benthic macroinvertebrates and bottom-feeding fish, the release of contaminants to the water column, bioaccumulation and biomagnification by benthic macroinvertebrates and bottom-feeding fish, and benthic macroinvertebrate species diversity and density was reviewed and summarized.

In Workplan B, BEAK screened the MOE In-Place Pollutants Program database, which contains information on metal and organic contaminant concentrations in whole sediments, sediment fractions, porewater and at the sediment-water interface; other physical-chemical sediment quality; contaminant concentrations in benthic macroinvertebrates and sculpins; and benthic macroinvertebrate community structure. A data set consisting of about 100 stations, based on the availability of tissue concentration data, was selected from the database and consolidated into a computer spreadsheet format for statistical analysis.

The data set was statistically analyzed to determine the factors (e.g., organic content, grain size) influencing the release to overlying water and bioavailability of contaminants in sediment, the degree of contaminant bioconcentration by benthic macroinvertebrates and sculpins, and the effects of sediment quality on benthic macroinvertebrate community structure.

The results of the statistical analysis, indicating relationships between different sediment quality parameters, between tissue concentrations and sediment quality parameters, and also between sediment quality and benthic macroinvertebrate community parameters, were interpreted, taking into account previously documented environmental relationships, so that, wherever possible, these relationships could be corroborated. In this manner, evidence for cause-effect relationships will provide a stronger basis for the derivation of sediment quality objectives in Phase II of this program.

In Workplan C, approaches to derivation of sediment quality objectives, which have been used or proposed for use by regulatory agencies, were collected from the literature and described. The availability of data required for application of each approach was determined for each contaminant, based on the database compiled in Workplan A, and on

screening of the MOE In-Place Pollutants Program database. A strategy for combined use of the various approaches in development of sediment quality objectives was proposed.



2.0 WORKPLAN A - DATA REVIEW AND EVALUATION

This section of the report provides a review and evaluation of data regarding the influence of contaminated freshwater sediments (with particular emphasis on the Great Lakes) on benthic macroinvertebrates and bottom-feeding fish, the release of contaminants to the water column, bioaccumulation and biomagnification by benthic macroinvertebrates and bottom-feeding fish, and benthic macroinvertebrate community structure.

2.1 Review of Sediment Toxicity Data

2.1.1 Sediment Toxicity Bioassay Methods

A number of bioassay methods have been developed to screen sediments from the field for acute and chronic toxicity. As discussed previously, the U.S. EPA/U.S. COE Technical Committee on Criteria for Dredged and Fill Material developed a sediment bioassay implementation manual (U.S. EPA/U.S. COE, 1977). It is the standard reference for regulatory testing of dredged material prior to marine open water or confined disposal. Basically, the procedures involve acute toxicity tests comparing the survival of sensitive aquatic organisms exposed to solid or liquid phases of candidate dredged material to the survival of those exposed to phases of uncontaminated reference sediments. Bioaccumulation potential is tested by analyzing tissues of surviving bioassay organisms after ten days exposure for elevated concentrations of contaminants. This evaluation protocol has been used for freshwater environments (e.g., Peddicord et al., 1980; Marking et al., 1981).

In the Great Lakes Basin, the U.S. Army COE, Buffalo District, has unilaterally embarked on a comprehensive program of acute toxicity testing of harbour and navigational waterway sediments using the mayfly nymph Hexagenia limbata, the waterflea Daphnia magna, and the fathead minnow Pimephales promelas. Testing is primarily based on a 96-hour bioassay procedure developed by Prater and Anderson (1977a, b) using a combination of the bulk chemical analysis procedure and percent mortality of test organisms for the evaluation of sediments.

Other similar bioassays for the assessment of acute and chronic toxicity of the solid sediment phase have been developed by Gannon and Beeton (1969, 1971), Tsai (1979), Bahnick et al. (1981a, b), Nebeker et al. (1984b) and Swartz et al. (1979, 1983). In these static bioassays, there is no variance of water:sediment ratios. In contrast, JBF (1978) used a range of water:sediment ratios in their static bioassay tests by maintaining a constant sediment area, but varying the volume of water over the sediment. The controlled variable in these tests was, therefore, not the suspected toxicant, but the diluent water. The ratio of volume of water to surface area of sediment was used to derive inferences regarding the toxicity of each sediment and to permit calculation of an LC50 value.

Bioassay testing can also involve the assessment of acute and chronic toxicity of the suspended sediment phase (e.g., LeGore and DesVoigne, 1973), as well as elutriate, interstitial and pore water phases (e.g., Shuba et al., 1977; Flint and Lorefice, 1978; Bahnick et al., 1981a; Munawar, 1982).

Other bioassay approaches have been developed, including selection (avoidance) of sediments by benthic macroinvertebrates (Gannon and Beeton, 1969, 1971; JBF, 1978; McMurtry, 1982), beating rates of fingernail clam (Musculium transversum) gill cilia (Anderson et al., 1978), bacterial bioluminescence assay (Schiewe et al., 1985), assay of in situ enzyme inhibition (Buikema et al., 1980), Ames' testing for mutagenic activity (Allen et al., 1983), and application of sediment extract on fish to assess neoplasia induction potential (Black, 1982, 1983). These and other toxicity testing protocols have been reviewed and evaluated by Craig (1984), Munawar et al. (1984) and BEAK/OCFANCHEM (1986).

2.1.2 Extent of the Sediment Toxicity Database

A considerable volume of data has been generated on the acute and chronic toxicity of contaminated sediments to benthic biota. Studies relating toxicity to benthic macroinvertebrates and bottom-dwelling fish of sediments with measured concentrations of specific contaminants are summarized in Tables 2.1 and 2.2, respectively. A review of these and other relevant studies is provided below.

TABLE 2.1: STUDIES RELATING TOXICITY TO BENTHIC MACROINVERTEBRATES OF SEDIMENTS WITH MEASURED CONCENTRATIONS OF SPECIFIC CONTAMINANTS

Contaminant	Species	Reference*
Cu, Zn	Tubifex tubifex Limnodrilus hoffmeisteri	McMurtry (1982, 1984)*
Cd, Cr, Cu, Fe, Pb, Mn, Hg, Ni, Zn	Hexagenia limbata	Malueg <u>et al.</u> (1984a)*
Cd, Cr, Cu, Pb, Hg, Ni, Zn	<u>Hexagenia</u> <u>limbata</u>	Malueg et al. (1984b)*
As, Cd, Cr, Cu, Fe, Pb, Mn, Hg, Ni, Zn	Hexagenia limbata Asellus communis	Prater and Hoke (1980)*
Cu	Chironomus decorus	Kosalwat and Knight (1987a, b)*
Cu	Chironomus tentans Hyalella azteca Gammarus lacustris	Cairns <u>et al.</u> (1984)*
Zn, PCB	Octolasion tyrtaeum Corbicula fluminea	Mac <u>et al.</u> (1984)*
Cd	Hyalella azteca	Nebeker <u>et al.</u> (1986a)*
Cd, Cr, Zn	Chironomus tentans	Wentsel et <u>al.</u> (1977a, b, 1978a, b)*
As, Cd, Cr, Cu, Fe, Pb, Mn, Hg, Ni, Zn, aldrin, β-BHC, γ-BHC, γ-Chlordane, ο,p-DDT, p,p-DDD, p,p-DDT, p,p-DDE, dieldrin, endrin, HCB, mirex, PCB	Hexagenia limbata Asellus communis	Prater and Anderson (1977b)*
As, Cd, Cr, Cu, Fe, Pb, Mn, Hg, Ni, Zn	Hexagenia limbata Asellus communis	Prater and Anderson (1977a)*
Cd, Cr, Cu, Fe, Pb, Hg, Ni, Zn, chlordane, DDD, DDE, DDT, dieldrin, endrin, PCB	Gammarus pseudolimnaeus Procambarus sp. Hexagenia sp. Chironomus tentans Physa gyrina Truncilla donaciformis Sphaerium sp.	Marking <u>et al.</u> (1980b)

TABLE 2.1: STUDIES RELATING TOXICITY TO BENTHIC MACROINVERTEBRATES OF SEDIMENTS WITH MEASURED CONCENTRATIONS OF SPECIFIC CONTAMINANTS

Contaminant	Species	Reference*
As, Cd, Cr, Cu, Fe, Pb, Mn, Hg, Ni, Zn, o,p-DDT, p,p-DDD, p,p-DDE, p,p-DDT, dieldrin, PCB	Palaemonetes kadiakensis	Shuba <u>et al.</u> (1978)
Cd, Cr, Cu, Fe, Pb, Hg, Ni, DDE, PCB	Gammarus fasciatus Procambarus sp. Hexagenia sp. Chironomus tentans Physa gyrina Truncilla donaciformis	Marking <u>et al.</u> (1980a)
Aldrin, chlordane, p,p-DDT, endrin, mirex	Stylodrilus heringianus Potamothrix vejdovski Limnodrilus hoffmeisteri	White (1984)*
Cd, Cr, Cu, Fe, Pb, Hg, Ni, Zn, chlordane, DDD, DDE, DDT, dieldrin, endrin, PCB	Gammarus pseudolimnaeus Procambarus sp. Hexagenia sp. Chironomus tentans Physa gyrina Truncilla donaci formis Sphaerium sp.	Marking <u>et al.</u> (1981)
As, Cd, Cr, Cu, Fe, Pb, Mn, Hg, Ni, Zn, DDE, PCB	Hexagenia limbata	Bahnick <u>et al.</u> (1981a)*
Hg, Zn	Pontoporeia affinis	Magnuson <u>et al.</u> (1976)*
PCB	Macrobrachium rosenbergii Corbicula fluminea	Tatem (1984)
Pb, Cd	Corbicula fluminea	Tatem (1984)
As, Cd, Cr, Cu, Fe, Pb, Mn, Hg, Ni, Zn, aldrin, β-BHC, γ-BHC, γ-chlordane, ο,p-DDT, pp-DDD, p,p-DDT, dieldrin, HCB, heptachlor, heptachlor epoxide, mirex, PCB	<u>Hexagenia limbata</u>	ABI (1982)
Нд, РСВ	Lumbricus terrestris	Mac and Willford (1986)

TABLE 2.1: STUDIES RELATING TOXICITY TO BENTHIC MACROINVERTEBRATES OF SEDIMENTS WITH MEASURED CONCENTRATIONS OF SPECIFIC CONTAMINANTS

Contaminant	Species	Reference*
As, Cd, Cr, Cu, Fe, Pb, Mn, Hg, Ni, Zn, aldrin, a-BHC, β-BHC, 7-BHC, chlordane, DDE, DDD, DDT, dieldrin, endrin, HCB, heptachlor, heptachlor epoxide, mirex, PCI	<u>Hexagenia limbata</u> B	ATEC (1983, 1984a*, b*, c*, 1985a, b, c*, d, e, 1986a, b*, c, d)
Cd, Pb, Hg, aldrin, β -BHC, γ -BHC, γ -chlordane, o,p-DDT, p,p-DDD, p,p-DDE, p,p-DDT, dieldrin, endrin, HCB, heptachlor, heptachlor epoxide, mirex, PCB	Hexagenia limbata Asellus intermedius	Recra (1981)
Cd, Cr, Cu, Pb, Ni, Zn, aldrin, α-BHC, β-BHC, chlordane, dieldrin, p,p-DDD, p,p-DDT, endrin, heptachlor, heptachlor epoxide	Hexagenia limbata Chironomus tentans , PCB	Chapman <u>et al.</u> (1986)*
As, Cd, Cr, Cu, Fe, Pb, Mn, Hg, Ni, Zn, aldrin, Y-BHC, DDT, dieldrin, heptachlor, heptachlor epoxide, PCB	Hyalella azteca Hexagenia limbata Truncilla donaciformis Amblema plicata	Peddicord <u>et al.</u> (1980)
As, Cd, Cu, Ni, Pb, Zn, PCB	Pontoporeia affinis	JBF (1978)*
As, Cd, Cr, Cu, Fe, Pb, Mn, Hg, Ni, Zn, aldrin, β-BHC, γ-BHC, γ-chlordane, ο,p-DDT, p,p-DDD, p,p-DDE, p,p-DDT, dieldrin, endrin, heptachlor, heptachlor epoxide, mirex, PC		EG&G Bionomics (1983)
As, Cd, Cr, Cu, Pb, Hg, Ni, Zn, aldrin, α -BHC, β -BHC, γ -BHC, chlordane, DDD, DDE DDT, dieldrin, endrin, HCB, heptachlor, heptachlor epoxide PCB	•	McFarland and Peddicord (1986)

^{*} Sediment contaminant concentration and sediment toxicity data in computer database (see Appendix 1).

TABLE 2.2:

STUDIES RELATING TOXICITY TO BOTTOM-DWELLING FISH SPECIES OF SEDIMENTS WITH MEASURED CONCENTRATIONS OF SPECIFIC CONTAMINANTS

Contaminant	Species	Reference*
As, Cd, Cr, Cu, Fe, Pb, Mn, Hg, Ni, Zn	Pimephales promelas	Prater and Hoke (1980)*
Cd, Hg, Zn	Carassius auratus	Birge et al. (1977)
Zn, PCB	Pimephales promelas	Mac <u>et al.</u> (1984)*
Cd	Carassius auratus	Francis <u>et al.</u> (1984)*
As, Cd, Cr, Cu, Fe, Pb, Mn, Hg, Ni, Zn	Pimephales promelas	Prater and Anderson (1977a)*
Fe, Pb, Hg, Ni, Zn	Gasterosteus aculeatus	LeGore and DesVoigne (1973)*
Hg, PCB	Pimephales promelas	Mac and Willford (1986)
As, Cd, Cr, Cu, Fe, Pb, Mn, Hg, Ni, Zn, aldrin, β-BHC, γ-BHC, γ-chlordane, ο,p-DDT, p,p-DDD, p,p-DDT, dieldrin, HCB, heptachlor, heptachlor epoxide, mirex, PCl		АБІ (1982)
As, Cd, Cr, Cu, Fe, Pb, Mn, Hg, Ni, Zn, aldrin, α-BHC, β-BHC, γ-BHC, chlordane, DDE, DDD, DDT, dieldrin, endrin, HCB, heptachlor, heptachlor epoxide, mirex, PCl	<u>Pimephales promelas</u>	ATEC (1983, 1984a*, b* c*, 1985a, b, c*, d, e, 1986a, b, c, d)
As, Cd, Cr, Cu, Fe, Pb, Mn, Hg, Ni, Zn, aldrin, β-BHC, γ-BHC, γ-chlordane, ο,p-DDT, p,p-DDD, p,p-DDE, p,p-DDT, dieldrin, endrin, heptachlor, heptachlor epoxide, mirex, PCI	•	EG&G Bionomics (1983)
As, Cd, Cr, Cu, Fe, Pb, Mn, Hg, Ni, Zn, aldrin, γ-BHC, DDT, dieldrin, heptachlor, heptachlor epoxide, PCB	<u>Ictalurus</u> <u>punctatus</u>	Peddicord <u>et al.</u> (1980)

TABLE 2.2: STUDIES RELATING TOXICITY TO BOTTOM-DWELLING FISH SPECIES OF SEDIMENTS WITH MEASURED CONCENTRATIONS OF SPECIFIC CONTAMINANTS

Contaminant	Species	Reference*
As, Cd, Cr, Cu, Pb, Hg, Ni, Zn, aldrin, α -BHC, β -BHC, γ -BHC, chlordane, DDD, DDE, DDT, dieldrin, endrin, HCB, heptachlor, heptachlor epoxide, PCB		McFarland and Peddicord (1986)

^{*} Sediment contaminant concentration and sediment toxicity data in computer database (see Appendix 1).

The actual sediment contaminant concentration and sediment toxicity data from most of these studies have been tabulated into a spreadsheet database format. An example of this database is presented in Appendix 1.

2.1.2.1 Sediment Toxicity to Benthic Macroinvertebrates

Great Lakes Studies

A number of studies have been undertaken to assess the acute and chronic effects of toxic contaminants in Great Lakes sediments on benthic macroinvertebrates.

For example, Gannon and Beeton (1969, 1971) carried out simple toxicity bioassays whereby the amphipod Pontoporeia affinis and the midge larva Chironomus tentans were exposed to a number of Great Lakes harbour sediments. All Buffalo sediments, the inner harbour samples from Calumet, the Cuyahoga River samples at Cleveland, all Indiana Harbor sediments, all Rouge River sediments, and a sample collected near the outfall of the Toledo sewage treatment plant were found to be toxic. Mortality was low or not significant (compared to off-shore controls) for sediments from the mouth of the Calumet River, the outer harbour of Calumet, Cleveland Harbor, Green Bay, Great Sodus Bay and Toledo. The sediments were not analyzed for specific contaminants.

Gannon and Beeton (1969, 1971) also carried out sediment selectivity experiments whereby P. affinis and C. tentans were exposed to a number of Great Lakes harbour sediments. The distribution of P. affinis in the test sediments showed a definite preference for open lake sediments rather than the harbour sediment test samples. For example, in one test trial, 62% (58 organisms) were recovered in the open lake sediments. The next highest density was six organisms in the Calumet outer harbour sediment sample. Four organisms were recorded from a Toledo sediment sample, and three from a Green Bay sample. Only one or two organisms were found in the other 13 sediment samples that contained P. affinis. However, 58% of the sediment samples (23 out of 40) did not have any P. affinis. Despite limited mobility, the midge larvae also showed preference for some sediments and avoided others. Certain sediments were avoided or resulted in high mortality of the test animals, and were obviously not suitable environments for either P. affinis or the more pollution-tolerant C. tentans. These sediment samples were from Buffalo, Calumet, Cleveland, Indiana Harbor, Milwaukee, Rouge River and Toledo.

JBF (1978) conducted similar sediment preference tests with Michigan City Harbor and open-lake sediments. P. affinis displayed greatest preference for open-lake sediments. However, the Michigan City Harbor sediments selected by P. affinis did not appear to adversely affect this species, since mortality was low or absent in the preference tests.

Oxberry et al. (1978) reported no adverse effects of continuous long-term (98- to 363-day) exposure to taconite tailings from a Lake Superior mining operation on the survival and condition of P. affinis and the amphipod Mysis relicta. In chemical terms, the tailings consisted of nearly 80% non-metallic elements (mostly silicon and oxygen), 15 to 17% iron and manganese, and 4 to 5% calcium, magnesium, sodium, potassium and aluminum. The tailings also contained relatively small amounts of heavy metals, notably copper, zinc and lead.

Based on toxicity bioassays, Malueg et al. (1984a) reported that mean mortality of the mayfly H. limbata was higher (16%) for sediment from the northern copper-impacted portion of the Keweenaw Waterway than for sediment from the southern, less impacted portion (8%); however, these values were not significantly different from controls (6.7%). For the test sediments from the northern and southern portions, copper concentrations ranged from 140 to 930 ug/g and 13 to 37 ug/g, respectively. Copper concentration in the control sediment was 200 ug/g. At the end of the ten-day exposure, copper concentrations overlying the northern portion test sediments ranged from 0.190 to 0.510 mg/L. The acute mortality data did not correlate with the absence of indigenous Hexagenia in the northern copper-impacted portion of the waterway. However, the tenday bioassay was designed only to indicate acute toxicity and would not detect long-term effects. It is conceivable that the absence of mayflies in the northern portion would be related to an inability of the organisms to complete their life cycle and maintain viable populations. In the same study, the northern portion test sediments were found to be generally acutely toxic to the water flea D. magna, based on 48-hour exposures run simultaneously with the H. limbata tests. In contrast, southern portion test sediments were not toxic to D. magna. Furthermore, Malueg et al. (1984b) reported that contaminated sediments (1,800 ug/g of copper) from Torch Lake in the Keweenaw Peninsula were highly toxic (mortality of 40%) to H. limbata (48-hour exposure). This mortality was significantly higher than that for the control (6.7%). Total copper concentration in the water during the test ranged from about 0.6 to about 1.2 mg/L.

Prater and Anderson (1977a) used a 96-hour sediment bioassay procedure to assess the pollution status of eight Duluth and Superior Harbor basin sediments using the mayfly nymph H. Iimbata and the isopod Asellus communis. Mortality (10 to 50%) of H. Iimbata occurred in six of the eight sediments. Mortality of A. communis (30%) was found to occur for one of two sediments. In a study of the same area, Bahnick et al. (1981a) reported that, based on 96-hour bioassays, survival of H. Iimbata exposed to Superior-Duluth Harbor sediments was significantly lower for only a small number of tests compared to controls. Prater and Hoke (1980) assessed the pollution status of ten Marinette-Menominee Harbor sediments. Mortality (10 to 60%) of H. Iimbata and A. communis occurred in nine of ten sediments and in all sediments, respectively.

Chapman et al. (1986) reported slightly elevated mortality of H. limbata (20%) exposed to Toledo Harbor sediments compared to the control (13%), whereas Toronto Harbour sediments produced considerable mortality in H. limbata (53%). The greater toxicity of Toronto Harbour sediment compared with Toledo Harbor sediment was confirmed by solid phase beaker tests. Mortality of midge larvae Chironomus sp. was four times higher in the Toronto sediments (87%) than in controls (23%), with Toledo sediment producing intermediate mortality (40%).

Prater and Anderson (1977b) reported extremely high mortalities of <u>A. communis</u> (100%) and <u>H. limbata</u> (70 to 100%) when exposed to three sediments from Otter Creek, which flows into Maumee Bay, Lake Erie. These sediments had elevated levels of oil and grease, COD, ammonia and several metals. A fourth sediment sample collected upstream and characterized by a more moderate pollution status elicited lower mortalities of <u>A. communis</u> (45%) and <u>H. limbata</u> (25%). In contrast, percent mortalities of <u>A. communis</u> and <u>H. limbata</u> exposed to control sediments were low (i.e., 5 and 0%, respectively).

A general review of the chemistry databases for these studies on harbour and Otter Creek sediments did not indicate that any one contaminant analyzed was responsible for mortality of the test organisms. The concentrations varied from one station to another, and did not always appear highest at those stations where mortality was greatest. It was assumed that either a synergistic effect was occurring which was lethal to the organisms, or contaminants that were not measured were present at concentrations eliciting mortality. However, Prater and Hoke (1980) did suggest that mortalities of test

organisms exposed to Marinette-Menominee sediments may be due to high levels of arsenic.

Relationships have been developed between percent mortality and chemical parameter data from bioassay tests of sediments from five Lake Michigan harbours (Indiana, Grand Haven, New Buffalo, Green Bay and Marinette-Menominee). Hoke and Prater (1980) reported that the mortality of H. limbata was significantly correlated with elutriate concentrations of chloride, ammonia and nickel. The empirical correlation of mortality and elutriate chemistry may have actually reflected the correlation of mortality with the release of chemical constituents of the sediments as measured by the difference chemical data (i.e., pre-test concentration value minus the post-test concentration value). Laskowski-Hoke and Prater (1981) found that H. limbata mortality was significantly and positively correlated with difference chemical data for chromium, cyanide and zinc (as well as ammonia), and suggested that this may illustrate an impairment of respiratory function. Laskowski-Hoke and Prater (1984) found positive correlations between the percent mortality of H. limbata and bulk sediment concentration of lead, iron, copper and chromium.

EG&G Bionomics (1983) reported that, based on a three-week exposure to test sediments from Cleveland Harbor, the emergence of adult midges <u>Paratanytarsus parthenogenica</u> was significantly reduced in one out of four sediment samples compared with control midge emergence. Average percent emergence was 56% for the control compared with 0% in the one test sediment. For the other three sediment samples, average percent emergence ranged from 61 to 78%. No relationship was readily evident between measured heavy metal concentrations in the four sediment samples and the chronic toxicity results. The concentrations of all specific organic contaminants measured were below the detection limits. However, oil and grease concentrations were markedly higher (16,000 ug/g) in the sediment sample eliciting the toxic response compared to levels in the other three samples (1.900 to 3.800 ug/g).

Using a flow-through bioassay system, Mac et al. (1984) tested sediments collected from the Raisin River near Monroe, Michigan for acute toxicity to the oligochaete worm Octolasion tyrtaeum, and the Asiatic clam Corbicula fluminea over a ten-day exposure. Oligochaete survival in the test sediment (100%) with 31.72 ug/g PCBs and 244 ug/g zinc was higher than that in the control sediment (94.6%) with 0.016 ug/g PCBs and 34 ug/g

zinc. Asiatic clam survival was 91.7% for both a test sediment containing 14.60 ug/g PCBs and 162 ug/g zinc, and a control sediment containing 0.014 ug/g PCBs and 67 ug/g zinc.

JBF (1978) conducted static bioassays of Michigan City Harbor sediments using P. affinis. A range of watersediment ratios was used by maintaining a constant sediment area, but varying the volume of water over the sediment. The controlled variable in these tests was, therefore, not the suspected toxicant, but the diluent water. The ratio of volume of water to surface area of sediment was used to derive inferences regarding the toxicity of each sediment and to permit calculation of an LC50 value. For the three sediments tested, maximum mortality ranged from 31 to 100% over 48 hours, and 37 to 96% over 96 hours. Correlations were found between the calculated LC50 values for P. affinis and the concentration of lead, cadmium and oil and grease in the test sediments. In contrast, a negative relationship was indicated for the LC50 values and sediment PCB concentrations. It was emphasized that these correlations may be spurious, and should not be used as evidence of the toxic effect of a particular contaminant. Many of the contaminants are highly intercorrelated. As a result, only one or two of the contaminants may be important, with the others implicated only circumstantially because of their correlation with the causative toxicants.

A considerable sediment toxicity database has been generated as a result of regulatory requirements (U.S. EPA/U.S. COE, 1977) to evaluate the suitability of dredged spoil for discharge into navigable ocean waters. The protocol tests for acute toxicity by comparing the survival of sensitive aquatic organisms exposed to candidate dredged material to the survival of those exposed to uncontaminated reference materials. The standard benthic macroinvertebrate test organism for acute toxicity testing of Great Lakes dredge material is the mayfly nymph <u>Hexagenia</u> (Revin, 1987). Other biota used as test organisms include the damselfly nymph (<u>Enallagma</u>), amphipods (<u>P. affinis</u> and <u>Gammarus</u>) and isopods (<u>Lirceus</u> and <u>Asellus</u>).

The Buffalo District of the U.S. Army COE has unilaterally initiated acute toxicity testing of dredge spoil material. Between 500 to 1,000 sediment samples have been tested for acute toxicity (Leonard, 1987). Toxicity testing of dredge spoil material has been undertaken infrequently by the Detroit and Chicago Districts (Jacek, 1987; Miller, 1987). The Chicago District has recently initiated a more comprehensive toxicity testing program based on bacterial bioluminescence and sponge recolonization assays for two

harbours (Waukegon, Calumet) to be undertaken jointly with the Illinois Natural History Survey, Champaign, Illinois,

BEAK was able to procure, from the Buffalo District, a number of reports on acute toxicity testing of dredge spoil material. Table 2.3 provides a summary of the 96-hour sediment bioassay test data. In general, the test sediments elicited a moderately elevated mortality response compared with the control, i.e., if survival of the test organism was over 90% in the control, survival in the test sediments was generally between 70 and 90%. In a number of cases, low percent survival in the test sediments reflected low percent survival in the control.

High mortality (i.e., survival less than 50%) compared with the control occurred for a relatively large number of test sediments from Sandusky Harbor (ATEC, 1980a, 1985c), Huron Harbor (ATEC, 1980a) and Conneaut Harbor (1980b). The high mortality results for Sandusky Harbor could not be readily related to any specific toxic contaminants in the sediments. The concentrations of the organic contaminants specifically addressed in this study were all below the analytical detection limit (Table 2.4). The concentrations of a number of polycyclic aromatic hydrocarbons (e.g., anthracene, benzo(a)anthracene, fluoranthene, phenanthrene) were generally above their detection limits. Toluene concentrations were also occasionally above the detection limit. No relationship was evident between the percent survival data and the concentrations of these organic contaminants above and below the detection limit. Heavy metal concentrations generally ranged from below to about two times above the guidelines for open-water disposal of dredge spoils (see Table 1.1).

Analytical data for the ten heavy metals addressed in this study are available for most of the sediment samples listed in Table 2.3. The metal concentrations are generally above the analytical detection limits. In contrast, as indicated in Table 2.4, the concentrations of organic contaminants are, with a few exceptions, consistently below the detection limits.

Other Studies

Using natural freshwater sediments spiked with copper, Cairns et al. (1984) conducted two static toxicity tests with a series of copper concentrations ranging from 59 to 10,600 ug/g. The first test showed a graded dose-response relationship for survival of the midge

		No. of Sar	No. of Samples with % Surviva	& Survival		
Location	No. of Samples Tested	%64-0	50-89%	90-100%	Control % Survival	Reference
Sandusky Harbor, Ohio	17	16	_	0	06	ATEC (1985c)
Oak Orchard Harbor, New York	7	0	7	0	06	ATEC (1984c)
Erie Harbor, Pennsylvania	9	0	0	9	86-46	ABI (1982)
Toledo Harbor, Ohio,	14	0	2	1.2	86	Recra (1981)
Toledo Harbor, Ohio¹	13	0	6	77	76-100	Recra (1981)
Toledo Harbor, Ohio	1.2	7	~	0	7.8	ATEC (1983)
Dunkirk Harbor, New York	13	13	0	0	41.7	ATEC (1986a)
Rochester Harbor, New York	14	0	14	0	8.7	ATEC (1985a)
Fairport Harbor, Ohio	17	0	17	0	8.5	ATEC (1986c)
Huron Harbor, Ohio	16	0	16	0	8.1	ATEC (1985d)
Erie Harbor, Pennsylvania	7	7	0	0	41.7	ATEC (1986d)
St. Lawrence River	6	3	9	0	99	ATEC (1985b)
Conneaut Harbor, Ohio	16	0	16	0	9.5	ATEC (1985e)
Port Clinton/West Harbor, Ohio	13	-	1.2	0	06	ATEC (1984b)
Cleveland Harbor, Ohio	17	0	17	0	98,3	ATEC (1986b)
Astabula Harbor, Ohio	15	0	15	0	46	ATEC (1984a)
Sandusky Harbor, Ohio*	1.2	01	2	0	06	ATEC (1980a)
Huron Harbor, Ohio*	10	9	3	0	9.2	ATEC (1980a)
Conneaut Harbor, Ohio*	=		10	0	7.5	ATEC (1980a)
Fairport Harbor, Ohio*	14	0	3	11	9.2	ATEC (1980a)
Huron Harbor, Ohio*	12			0	88,3	ATEC (1980b)
Conneaut Harbor, Ohio*	10	7	2	-	06	ATEC (1980b)

Test species was Asellus intermedius.

^{*} No bulk chemical sediment data available.

				Concentra	Concentration Range (ug/g)	(g/gn)			
Organic Contaminant	Sandusky (A TEC, 198 &)	Oak Orchard (ATEC, 1984b)	Erie (ABI, 1982)	Toledo (Recra, 1981)	Toledo (ATEC, 1983)	Toledo (ATEC, 1986a)	Rochester (ATEC, 1985a)	Fairport (ATEC, 1986c)	Huron (ATEC, 1983d)
Aldrin	L* 0.01	1, 0,01	L 1	L 0.05	L 0.01	L 0.01	L 0.01	L 0.01	L 0.01
a -BHC	L 0.01	L 0.01	**N/A	N/A	L 0.01	L 0.01	L 0.01	L 0.01	L 0.01
β-BHC	L 0.01	L 0.01	L 1	L 0.01	L 0.01	L 0.01	L 0.01	L 0.01	L 0.01
γ-BHC	L 0.01	L 0.01	L 2	L 0.01	L 0.01	L 0.01	L 0.01	L 0.01	L 0.01
Chlordane	L 0.10	L 0.10	L 2	L 0.03	L 0.10	L 0.10	L 0.10	L 0.10	L 0.10
o,p-DDT	A/N	N/A	L 3	L 0.01	N/A	N/A	N/A	N/A	N/A
p,p-DDE	L 0.02	L 0.02	L 1	L 0.01	L 0.02	L 0.02	L 0.02	L 0.02	L 0.02
D.pDDD	L 0.02	L 0.02	r 3	L 0.02	L 0.02	L 0.02	L 0.02	L 0.02	1 0.02
p,p'-DDT	L 0.02	L 0.02	L 3	L 0.01	L 0.02	L 0.02	L 0.02-0.031***	1 0.02	L 0.02
Dieldrin	1 0.02	L 0.02	L 2	L 0.02	L 0.02	L 0.02	L 0.02	L 0.02	L 0.02
Endrin	L 0.03	L 0.03	N/A	L 0.02	L 0.03	L 0.03	L 0.03	L 0.03	L 0.03
HCB	L 0.7	N/A	L 2	L 0.01	0 0°40	N/A	N/A	N/A	L 0.7
Heptachlor	L 0.02	L 0.02	1 1	L 0.05	L 0.02	L 0.02	L 0.02	L 0.02	L 0.02
Heptachlor Epoxide	L 0.03	L 0.03	L 2	L 0.01	L 0.03	L 0.03	L 0.03	L 0.03	L 0.03
Mirex	L 0.05	L 0.05	L 3	L 0.05	L 0.05	N/A	L 0.05	N/A	L 0.05
PCB (by Aroclor)	L 0.1	L 0.10	L 2	L 0.1-L 0.2	L 0.10	1 0.10	L 0.1	L 0.10	L 0.1

L = less than.

^{***} Superscript number indicates number of samples above the detection limit (for total number of samples analyzed, see Table 2.3). ** N/A = not analyzed.

	Ashtabula Cleveland (ATEC, (EG&G Bionomics, 1984a) 1983)		-		L 0.01	L 0.01 L 0.2	L 0.10 N/A	N/A L 0.3	L 0.02 L 0.1	L 0.02 L 0.3	L 0.02 L 0.3	L 0.02 L 0.2	L 0.03 N/A	L 0.01-0.65 ¹³ N/A	L 0.02 L 0.1	L 0.03 L 0.2	
(8/8r	Cleveland (ATEC, 1986b)	-	L 0.01	10.01	L 0.01	L 0.01	L 0.10	A/A	L 0.02-0.08 ⁴	L 0.02-1.18 ¹	L 0.02	L 0.02	L 0.03	A/X	L 0.02	L 0.03	Α/Ν
Concentration Range (ug/g)	Port Clinton ATEC, 1984b)	-	1 0 01 0 05 1***	L 0.01-0.03 ***	L 0.01	L 0.01-0.031	L 0.10	N/A	L 0.02-0.042	L 0.02-0.06 ²	L 0.02-0.40 ³	L 0.02	L 0.03	L 0.40	L 0.02	L 0.03	5001
Con	Conneaut ATEC, 1985c)		10.01	L 0.01	L 0.01	L 0.01	L 0.10	N/A	L 0.02	L 0.02	L 0.02	L 0.02	L 0.03	L 0.7	L 0.02	L 0.03	1001
	St. Lawrence (ATEC, 19835)	-	10:01	10.01	L 0.01	L 0.01	L 0.10	N/A	L 0.02	L 0.02	L 0.02-0.03 ¹	L 0.02	L 0.03	N/A	L 0.02	L 0.03	1 0 0 5
	Erie (ATEC, 1986d)		1001	L 0.01	L 0.01	L 0.01	L 0.10	N/A**	L 0.02	L 0.02	L 0.02	L 0.02	L 0.03	N/A	L 0.02	L 0.03	A/N
	Organic Contaminant	Aldein	Violini BHD	4 - DHC	β-BHC	7 -BHC	Chlordane	o,p-DDT	p,p-DDE	p,p-DDD	p,p'-DDT	Dieldrin	Endrin	HCB	Heptachlor	Heptachlor Epoxide	Mirex

^{*} L = less than.

^{**} N/A = not analyzed.

^{***} Superscript number indicates number of samples above the detection limit (for total number of samples analyzed, see Table 2.3).

larva <u>C. tentans</u>, with a ten-day LC50 of 2,296 ug/g of copper (based on dry-weight sediment). A graded dose-response relationship was also exhibited in the second test using a different source sediment. Based on dry-weight sediment copper concentrations, the ten-day LC50 values were 964 ug/g for the amphipod <u>Gammarus lacustris</u>, 1,078 ug/g for the amphipod <u>Hyalella azteca</u> and 857 ug/g for <u>C. tentans</u>. The different LC50 values in the two tests with <u>C. tentans</u> probably reflect the different composition of the two test sediments and the ability of the sediment constituents to bind and hold copper. Based on soluble copper concentrations in overlying water in the second test, ten-day LC50 values were 61 ug/L for <u>G. lacustris</u>, 37 ug/L for <u>H. azteca</u> and 38 ug/L for <u>C. tentans</u>. All of the observed toxicity in this test could be accounted for by soluble copper, because the LC50 values were very similar to those obtained in waterborne copper bioassays. Little, if any, of the toxicity could be attributed to sediment-bound copper.

Kosalwat and Knight (1987b) exposed fourth instar larvae of the midge Chironomus decorus to copper in food-substrate (Cerophyl, dehydrated unjointed rye cereal and grass leaves). From preliminary tests, C. decorus was found to be very tolerant to copper spiked food-substrate. The substrate had to be spiked with a copper level as high as 4,000 ug/g before larval mortality was recorded over 72 hours. The Cerophyl was capable of adsorbing or more likely combining with copper up to a maximum concentration of 7,800 ug/g. The 72-hour LC 50 value was determined to be 5,830 ug/g of copper in Cerophyl. Copper concentrations in the overlying water increased with increasing concentrations in the Cerophyl. For example, concentrations of 87 and 428 ug/L copper were measured in the water overlying Cerophyl with copper concentrations of 4,608 and 7,533 ug/g, respectively. Based on acute toxicity tests with aqueous and substrate-bound copper, it was concluded that copper was more toxic to midges when present as a waterborne form than when present in the food-substrate (organically complexed forms).

Kosalwat and Knight (1987a) reported that growth of <u>C. decorus</u> larvae from the age of one to 15 days old was reduced significantly when reared in copper-spiked food-substrate (Cerophyl) with a concentration range of 900 to 4,500 ug/g. The substrate copper concentration at which larval growth was reduced to 50% was 1,602 ug/g. Furthermore, substrate copper concentration higher than 1,800 ug/g delayed adult emergence. Larvae reared in the two highest concentrations of substrate copper (3,478 and 4,302 ug/g) never emerged, having all died before pupating.

Nebeker et al. (1986a) spiked freshwater sediments and water with cadmium to determine if cadmium in the sediment would cause increased toxicity to the amphipod H. azteca. Test exposures were 2.5, 5.0, 10, 20 and 40 mg cadmium added to 800 mL of water and 200 mL of sediment. Sediment cadmium concentrations were not reported. The 96-hour LC50 value for a test without sediment was 8 ug/L total cadmium; two tenday LC50 values were less than 2.8 and 6.0 ug/L. For tests with sediment, the 96-hour LC50 values for total and soluble cadmium in water above the sediment were 74 and 6.6 ug/L, respectively. The ten-day LC50 for total cadmium in the test was 80 ug/L, similar to the 96-hour LC50 for total cadmium, indicating that little additional mortality occurred after 96 hours. The higher LC50 values for total cadmium indicate that much of cadmium in tests with sediments is likely bound to particulate and soluble organic materials, making it unavailable to exert a toxic effect on the organisms.

Magnuson et al. (1976) exposed the amphipod P. affinis to sediments enriched with mercury or zinc to determine mortality during two- and five-day exposures. Survival of P. affinis on mercury-treated sediments was similar to that on control sediments. Mercury concentrations in the spiked sediments ranged from 0.65 to 1.15 ug/g for the two-day exposures, and 2.15 to 3.35 ug/g for the five-day exposures. Mercury concentrations in the control sediments were 0.05 ug/g and 0.01 ug/g, respectively, for the two exposures. Similarly, survival of P. affinis on zinc-treated sediments was not different than that on control sediments. Zinc concentrations in the spiked sediments ranged from 68 to 99.5 ug/g for the two-day exposures, and 58.5 to 123.5 ug/g for the five-day exposures. Zinc concentrations in the control sediments ranged from 13 to 26 ug/g.

White (1984) reported on preliminary results of acute and chronic toxicity of a number of organic contaminants in sediments on oligochaete worms. Based on 96-hour toxicity tests, <u>Stylodrilus heringianus</u> showed no mortality in sediment spiked with concentrations of 2,4,5,2',4',5'-hexachlorobiphenyl (HCBP) up to 1,000 ug/g. HCBP concentrations greater than 0.075 ug/g did restrict or limit burrowing and fecal pellet evolution in <u>Potamothrix vejdovski</u>, but had little or no effect on <u>S. heringianus</u> or <u>Limnodrilus hoffmeisteri</u>. Fecal pellet evolution for <u>L. hoffmeisteri</u> in 175 ug/g HCBP was equal to or greater than in controls.

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Sediment reworking by <u>S. heringianus</u> was greatly reduced in sediments containing 75 ug/g endrin while, at 0.050 ug/g, it was significantly enhanced relative to control values (White, 1984). Reworking rates in intermediate concentrations (0.5 and 5 ug/g) were initially faster than controls then significantly slowed after 300 hours.

White (1984) also conducted 96-hour exposure tests on <u>S. heringianus</u> to aldrin, p,p-DDT, chlordane, endrin and mirex at concentrations of 0.005 and 1,000 ug/g in sediments. At the low concentration, percent survival after 96 hours was 30% for mirex, 60% for chlordane or p,p-DDT, and 100% for aldrin or endrin. At the high concentration, percent survival was 0% for chlordane, again 30% for mirex, 40% for aldrin with no burrowing activity, 40% for endrin with the worms unhealthy and exhibiting no burrowing activity, and 50% (20% worms healthy, 30% unhealthy) for p,p-DDT with some burrowing activity. Based on further testing of endrin toxicity on <u>S. heringianus</u>, burrowing was retarded between 1 and 75 ug/g, the worms became unhealthy between 100 and 200 ug/g, and the approximate 96-hour LC50 value was 1,000 ug/g of endrin in sediment.

As part of a series of laboratory studies on the role of contaminated sediment in the sublethal or lethal effects of trace metals in benthic macroinvertebrates, Wentsel et al. (1977a) exposed chironomid larvae (C. tentans) for 17 days to five sediments from Palestine Lake, Indiana with varying concentrations of heavy metals. The control sediment had levels of 0.6 ug/g cadmium, 17 ug/g chromium and 77 ug/g zinc, whereas the two most contaminated sediments had levels up to 1,030 ug/g cadmium, 2,130 ug/g chromium and 17,300 ug/g zinc. Survival of the chironomid larvae ranged from 46% in the most contaminated sediment to 81% in the control sediment, with the difference in survival between the control and most contaminated sediment being statistically significant. In addition, the mean length and weight of the larvae from the control sediment were 1.83 cm and 2.86 mg, respectively. In contrast, the mean length and weight of larvae from the most contaminated sediment were only 0.82 cm and 0.20 mg, respectively. A linear relationship was found for the square root of length versus metal levels in the sediment, indicating that these metals are a likely cause for the inhibition of chironomid larvae development.

These survival and growth data explain why chironomids were not found in areas of highly contaminated sediment in Palestine Lake (Wentsel et al., 1977a). Furthermore, Wentsel et al. (1978a) reported that, during a 14-day exposure, emergence of chironomid larvae

was reduced by over three times and delayed for two days in the most contaminated sediment compared with the control. It was also determined that the chironomids actively avoided sediments with high levels (Wentsel et al., 1977b); thus, they may migrate from highly contaminated areas in order to mature.

Wentsel et al. (1978b) reported evidence of the development of resistance to metals by chironomid larvae. Larvae collected from the contaminated and uncontaminated areas of Palestine Lake were exposed for 96 hours to a highly contaminated sediment, containing 1,070 ug/g cadmium, 15,100 ug/g zinc and 1,680 ug/g chromium. Larval survival was only 47.5% for those of uncontaminated sediment origin, whereas 75% of the larvae collected from the contaminated area survived. Percent survival of two groups of chironomids was significantly different, indicating that the larvae from the contaminated area of the lake may be, to some degree, resistant to heavy metal pollution. Based on five-day avoidance response experiments providing uncontaminated and contaminated sediment in each half of an aquarium tank, 76% of the uncontaminated source area chironomids were found in the uncontaminated sediment, whereas only 33% of the contaminated source area chironomids were found there. These data also suggested that an insensitivity or resistance to the heavy metals has developed in the chironomids from the contaminated area of the lake. Finally, growth experiment data indicated an overall increase in length of 8,8% for uncontaminated source area chironomids compared with 18% for contaminated source area chironomids, exposed to sediments containing 657 ug/g cadmium, 8,280 ug/g zinc and 1,080 ug/g chromium,

Sediments from the Phillips Chain of Lakes in Wisconsin were tested by Malueg et al. (1984b) for acute toxicity using the mayfly nymph H. limbata. None of the test sediment mortalities (6,7 to 13.3%) over the ten-day exposure were significantly different from the control (6.7%). The most contaminated test sediment contained 4.9 ug/g cadmium, 540 ug/g copper, 9.4 ug/g mercury, 350 ug/g nickel, 160 ug/g lead and 570 ug/g zinc. Only chromium and copper were found in the overlying water in detectable amounts (maximum concentrations of 225 and 110 ug/L, respectively).

Malueg et al. (1984b) also tested sediments from the Little Grizzly Creek System for acute toxicity using H. limbata. This stream receives the drainage from one of California's most productive copper mines which operated during the first half of this century. Mortalities for all mine-impacted test sediments (93,3 to 100%) were

significantly greater than that of the control (6.7%). In contrast, mortalities in the two non-impacted test sediments (13.3 to 20.0%) from this drainage system were not significantly different from that of the control. Bulk sediment copper concentrations varied with distance downstream of the mine from 2,700 to 550 ug/g in the test sediments. Test sediments from the two non-impacted stations, above the mine and above the confluence of the impacted creek, had copper concentrations of 60 and 16 ug/g, respectively. Furthermore, copper was the only toxic metal present in the overlying test water in detectable quantities (up to 3,500 ug/L).

Magnuson et al. (1976) reported that concentrations of mercury between 0.6 and 3.0 ug/g in sediments affected the activity behaviour of the amphipod P. affinis, with a decline in the number of active animals and decreased activity rates. In contrast, zinc concentrations between 58.5 and 123.5 ug/g in sediments did not cause a change in the numbers of active P. affinis; however, their rate of activity was significantly lower compared to controls.

A number of studies have demonstrated avoidance reactions of benthic invertebrates to contaminated sediments. For example, Wentsel et al. (1977b) established a linear relationship between cadmium and zinc concentrations in sediments and avoidance by the midge larva C. tentans. An approximate threshold avoidance of metals in the sediments was determined to be 213 to 422 ug/g of cadmium, 4,385 to 8,330 ug/g of zinc, and 799 to 1,513 ug/g of chromium. McMurtry (1984) reported an avoidance response of tubificid oligochaetes Tubifex tubifex and L. hoffmeisteri to dosed Toronto Harbour sediment containing sublethal concentrations of copper (570 ug/g) and zinc (1,135 ug/g) alone, or copper (550 ug/g) and zinc (1,080 ug/g) in combination. The effect of copper and zinc in combination was not significantly greater than that of either metal alone.

As part of his avoidance studies, McMurtry (1982) conducted 96-hour static toxicity tests to determine concentrations of copper and zinc in sediment that caused no acute mortality to T.tubifex and L.tubifex and zinc (1,300 ug/g) alone, or copper (625 ug/g) and zinc (1,300 ug/g) alone, or copper (625 ug/g) and zinc (1,360 ug/g) in combination. Copper concentrations (0.078 mg/L) in the water overlying the test sediments spiked with copper was below the 48-hour LC50 value of 0.89 mg/L copper for L.tubifex (Brkovic-Popovic and Popovic, 1977a). Zinc

concentration (2.69 mg/L) in overlying water of the sediment zinc exposure was also below the 48-hour LC50 value of 60.2 mg/L zinc (Brkovic-Popovic and Popovic, 1977a). Copper (0.053 mg/L) and zinc (7.54 mg/L) concentrations in the water overlying sediment spiked with both copper and zinc were also below the respective LC50 values for T. tubifex.

As indicated in Section 2.1.1, sediment bioassay testing has been undertaken by the U.S. Army COE to evaluate potential impacts of dredging and disposal operations and/or the suitability of dredge spoil for discharge in freshwater environments. Reports on such studies outside of the Great Lakes, as Peddicord et al. (1980) and Marking et al. (1981) for the Upper Mississippi River, and Marking et al. (1980a, b) for the Lake of the Woods, were available, but not reviewed as part of this project. The concurrent data for benthic macroinvertebrate toxicity and bulk sediment chemical composition in these and other U.S. Army COE reports should be reviewed for the development of numerical sediment quality criteria for specific contaminants (Phase II of this study).

2.1.2.2 Sediment Toxicity to Fish

Fewer studies have been undertaken to assess the acute and chronic effects of toxic contaminants in sediments on fish (Table 2.2) compared to studies using benthic macroinvertebrates (Table 2.1).

Great Lakes Studies

Oxberry et al. (1978) reported no adverse effects of long-term (22 to 49 days) continuous exposure to taconite tailings from a Lake Superior mining operation on the survival and condition of juvenile rainbow trout (<u>Salmo gairdneri</u>), brook trout (<u>Salvelinus fontinalis</u>) and yellow perch (<u>Perca flavescens</u>). No adverse effects were also noted on the hatching of eyed eggs of rainbow trout and lake trout, or on the survival of the hatched larvae (sac fry), based on exposures of 84 to 119 days.

Based on the 96-hour sediment bioassay procedure, Prater and Anderson (1977a) assessed the pollution status of eight Duluth and Superior Harbor basin sediments using the fathead minnow (<u>Pimephales promelas</u>) as a test organism. Mortality (10%) was found to occur for two of the eight sediments. Similarly, Prater and Hoke (1980) assessed the

pollution status of ten Marinette-Menominee Harbor sediments. Mortalilty (10%) occurred for only one of the ten sediments.

Using a flow-through bioassay system, Mac et al. (1984) tested sediments collected from the Raisin River near Monroe, Michigan for acute toxicity to the fathead minnow and the yellow perch over a ten-day exposure. Fathead minnow survival in the test sediment (100%) with 31.72 ug/g PCBs and 244 ug/g zinc was higher than that in the control sediment (95%) with 0.016 ug/g PCBs and 34 ug/g zinc. Yellow perch survival was 100% for both the test sediment containing 12.78 ug/g PCBs and 147 ug/g zinc and the control sediment containing 0.013 ug/g PCBs and 31 ug/g zinc.

As discussed previously, the Buffalo District of the U.S. Army COE has undertaken considerable acute toxicity testing of dredge spoil material. The standard fish test organism is the fathead minnow (P. promelas). Table 2.5 provides a summary of the 96-hour sediment bioassay test data obtained from the Buffalo District. In general, the majority (70%) of the test sediments elicited no elevated mortality response compared with the control, i.e., if survival was 90% or higher in the control, survival in most of the test sediments was 90% or higher. The rest of the test sediments elicited a moderately elevated mortality response, generally between 70 and 90%. In one study (ATEC, 1985d), low percent survival in the test sediments reflected low percent survival in the control.

Contaminant concentration data are available for most of the sediment samples listed in Table 2.5. However, as indicated in Table 2.4, the concentrations of organic contaminants are, with a few exceptions, consistently below the detection limits.

Bahnick et al. (1980a) conducted fish breathing response bioassays to assess the effects of interstitial water from Superior-Duluth Harbor sediments. In the bioassay, both cough frequency and the percentage of time opercular activity took place were recorded in bluegill (Lepomis macrochirus) exposed to dechlorinated city water (control), 10% interstitial water and 25% interstitial water. Cough rates were significantly higher than background frequencies with interstitial mixtures for three of six sediment samples, and significantly lower than background for one sediment sample. These differences in cough rates may have been due to chemical differences between test mixtures or observation time (cough frequencies were found to vary considerably during the test duration). The percentage of the time opercular activity occurred was significantly lower for five of the six test samples compared to that in the control.

		No. of Samples with % Survival	oles with %	Survival		
Location	No. of Samples Tested	%67-0	50-89%	20-89% 90-100%	Control % Survival	Reference
Sandusky Harbor, Ohio	17	0	9	1.1	116	ATEC (1985c)
Oak Orchard Harbor, New York	7	0	7	0	4.16	ATEC (1984c)
Eric Harbor, Pennsylvania	9	0	0	9	98-100	ABI (1982)
Toledo Harbor, Ohio	12	0	2	10	100	ATEC (1983)
Toledo Harbor, Ohio	13	0	0	13	100	ATEC (1986a)
Rochester Harbor, New York	14	0	9	~	100	ATEC (1985a)
Fairport Harbor, Ohio	17	0	11	9	06	ATEC (1986c)
Huron Harbor, Ohio	16	Ξ	~	0	1.5	ATEC (1985d)
Erie Harbor, Pennsylvania	7	0	0	7	100	ATEC (1986d)
St. Lawrence River	6	0	3	9	84	ATEC (1985b)
Conneaut Harbor, Ohio	16	0	3	13	86	ATEC (1985e)
Port Clinton/West Harbor, Ohio	13	0	2	∞	26	ATEC (1984b)
Cleveland Harbor, Ohio	17	0	1.5	2	86.7	ATEC (1986b)
Ashtabula Harbor, Ohio	15	0	-	14	100	ATEC (1984a)
Cleveland Harbor, Ohio	77	0	†7	0	48	EG&G Bionomics (1983)
Sandusky Harbor, Ohio*	12	0	2	01	100	ATEC (1980)
Huron Harbor, Ohio*	10	0	0	10	100	ATEC (1980)
Conneaut Harbor, Ohio*	=	0	0	Ξ	95	ATEC (1980a)
Fairport Harbor, Ohio*	14	0	0	14	95	ATEC (1980a)
Huron Harbor, Ohio*	12	0	6	3	100	ATEC (1980b)
Conneaut Harbor, Ohio*	01	0	8	2	98.3	ATEC (1980b)

^{*} No bulk chemical sediment data available.

Other Studies

Birge et al. (1977) evaluated the embryopathic effects of cadmium, mercury and zinc released from metal-enriched sediments on goldfish (Carassius auratus). Sediments were enriched with each metal at four enrichment levels starting at 0.1 ug/g and increasing at ten-fold intervals to 100 ug/g. Exposure was initiated after fertilization and maintained through four-days post-hatching. Toxicity results are presented as frequency of percent mortality in the metal-enriched bioassays over that in the control bioassays. Percent mortality in the control was not given. For all test bioassays of spiked sediments, embryonic mortality was appreciably higher than for the controls. However, no relationship was evident between the frequency of percent mortality and increasing sediment metal concentration over the range tested.

In contrast, a distinct inverse correlation was found between metal concentration and percent survival of rainbow trout (<u>S. gairdneri</u>) at hatching and at ten-days post-hatching (Birge <u>et al.</u>, 1977). For example, in trout bioassays on mercury-spiked sediment, survival values at ten-days post-hatching were 70, 45 and 0% for enrichment levels of 0.1, 1.0 and 100 ug/g, respectively. Survival values for cadmium-spiked sediment were 80, 53 and 11% at enrichment levels of 0.1, 1.0 and 100 ug/g, respectively. Zinc was less toxic, with survival values of 88, 56 and 28% at enrichment levels of 1, 100 and 1,000 ug/g, respectively. In contrast, survival at ten-days post-hatching was 94% for control bioassays. In general, the concentrations of metals in the overlying water increased with increasing sediment metal concentrations.

Francis et al. (1984) also evaluated the effects of cadmium-enriched sediment on embryo-larval stages of the goldfish (C. auratus). Natural stream sediment was enriched with cadmium to nominal concentrations of 1, 10, 100 and 1,000 ug/g. Fertilized eggs were maintained through four-days post-hatching, providing a total exposure time of six to seven days. The cadmium concentrations ranged from 2.2 to 68.6 ug/L in the water above sediments containing 1 to 1,000 ug/g, respectively. There was no significant reduction in survival compared with the control. A survival frequency of 98% was recorded for goldfish exposed to the cadmium concentration of 68.6 ug/L in water. This high survival was not expected when the reported LC50 concentration is 170 ug/L. The data suggested that sediment-released cadmium may be less toxic than free aqueous cadmium ion (Cd²⁺). Schuytema et al. (1984) hypothesized that Cd²⁺ is the predominant

toxic species, so that its complexation with suspended or dissolved organic matter derived from sediments results in reduced toxicity.

Francis et al. (1984) also reported largemouth bass (Micropterus salmoides) survival ranged from 75% at 1,000 ug/g to 95% at 10 ug/g. This reduction in survival at the highest sediment cadmium concentration was statistically significant. In contrast to the goldfish results, the toxicity observed in the test with bass was greater than that which would have been predicted from the reported LC50. The cadmium concentration of 43.9 ug/L in the water overlying the test sediment with 1,000 ug/g cadmium was less than 3% of the reported LC50 (1,640 ug/L). An important difference between the bass test and the goldfish bioassay was that bass eggs and larvae had direct contact with the sediment throughout the exposure period, whereas the goldfish stages remained in the water column above the sediment during much of the test. Because of this extended contact time with contaminated sediment, bass embryos may have been exposed to much higher cadmium levels than were measured in the overlying water.

LeGore and DesVoigne (1973) conducted static 96-hour bioassays exposing threespine sticklebacks (Gasterosteus aculeatus) to suspensions of sediment (doses of up to 5% wet weight) from the Duwamish Waterway, Seattle, Washington. No observable effect on the fish was observed. Metal concentrations in the sediments tested ranged from 0.04 to 0.13 ug/g mercury, 10 to 59 ug/g lead, 122 to 201 ug/g zinc, 27 to 30 ug/g nickel and 9,000 to 42,000 ug/g iron.

As discussed previously, a number of U.S. Army COE reports were available that provided sediment bioassay testing results for freshwater environments outside of the Great Lakes, e.g., the Upper Mississippi River (Peddicord et al., 1980; Marking et al., 1981) and the Lake of the Woods (Marking et al., 1980a, b). These reports were not reviewed as part of this project. However, the concurrent data for fish toxicity and bulk sediment chemical composition in these and other U.S. Army COE reports should be reviewed for the development of numerical sediment quality criteria for specific contaminants (Phase II of this study).

2.1.2.3 Factors Affecting Sediment Toxicity

A number of studies have indicated that sediments themselves generally modify the toxicity of contaminants (e.g., Chapman et al., 1982a; Nebeker et al., 1986a; Burton et

al., 1987). Sorption processes bind heavy metals and organic substances, providing a detoxification mechanism. Contaminant concentrations generally have to reach extremely high levels in sediment before acute toxic effects are elicited in benthic biota. For example, Francis et al. (1984) found no significant mortality of goldfish exposed to sediment enriched with cadmium to a concentration of 1,000 ug/g. White (1984) reported a 96-hour LC50 value of 1,000 ug/g endrin in sediment for the oligochaete worm S. heringianus. Cairns et al. (1984) reported ten-day LC50 values of 2,296 and 857 ug/g of sediment copper for the midge larvae C. tentans.

The difference in the LC50 values for copper found by Cairns et al. (1984) probably reflected the different composition of the two sediments tested and the ability of the sediment constituents to bind and hold copper. The sorption capacity of sediments and factors affecting chemical release are discussed in detail in Section 2.2.

For metals, it would appear that toxic effects apparently occur when the metal is mobilized from the solid (sediment) phase to the liquid (water) phase, from which they are readily taken up by aquatic biota. This liquid phase may be interstitial or pore water, or the water overlying the sediment. The relative distribution of the metal between the two phases is controlled by equilibrium kinetics. Higher sediment contaminant concentrations result in higher liquid phase contaminant concentrations.

Therefore, Cairns et al. (1984) have proposed that the solid-phase LC50 values for a metal are simply the sediment metal concentrations that correspond to the LC50 value for the waterborne metal (liquid phase) at equilibrium for a given sediment type. As a result, it was suggested that water quality standards applied near the sediment-water interface or in interstitial waters may perhaps adequately protect aquatic life.

Furthermore, metals appear to be significantly more toxic when present in a waterborne form than when present in the food-substrate (organically complexed form). For example, Kosalwat and Knight (1987b) reported that copper in a food-substrate (Cerophyl) had to reach an extremely high level (e.g., 4,000 ug/g) before it produces acute toxic effects. However, over an extended period, low levels of metals in sediment-associated food-substrate may produce chronic toxic effects on aquatic organisms in terms of growth reduction, life cycle alteration, reduced resistance to diseases, and deformities.

Schuytema et al. (1984) hypothesized that the free aqueous cadmium ion is the predominant toxic species so that its complexation with suspended or dissolved organic matter derived from sediments results in reduced toxicity. Similarly, Nebeker et al. (1986a) reported that mortality of the amphipod H. azteca was similar in tests with and without cadmium-spiked sediment. The water-only 96-hour LC50 value was 8 ug/L total cadmium, whereas two ten-day LC50 values were less than 2.8 and 6.0 ug/L. The 96-hour LC50 values for total and soluble cadmium in water above the sediment were 74 and 6.6 ug/L, respectively. The ten-day LC50 for total cadmium was 80 ug/L, similar to the 96hour LC50 for total cadmium, indicating that little additional mortality occurred after 96 hours. The higher LC50 values for total cadmium indicate that much of the cadmium is bound to particulate and soluble organic materials, making it unavailable to exert an acutely toxic effect on the organisms. Cairns et al. (1984) also suggested that various copper complexes and precipitates are generally not toxic, and tend to mask and remove the toxicity ascribed to copper. Therefore, for metals, it may be more appropriate to consider soluble ionic concentration rather than total recoverable concentration in the liquid phase to evaluate toxicity potential.

For the organochlorine contaminants addressed in this study, food chain uptake is likely a significant mode for the expression of toxicity. This is due to their hydrophobic nature resulting in extremely low concentrations in water. Bioaccumulation of contaminants from sediment and water is discussed in detail in Section 2.3.

Modifying factors affecting toxicity of waterborne contaminants are discussed in Section 2.1.3.3.

2.1.3 Extent of Waterborne Toxicity Database

2,1,3,1 Toxicity to Benthic Macroinvertebrates

A considerably larger database is available on the toxicity of contaminants in water to benthic macroinvertebrates compared to that for contaminants in sediment. Appendix 2 provides readily available toxicity data for the contaminants addressed in this study. This database for toxicity of waterborne contaminants to benthic macroinvertebrates provides a basis for the formation of a more comprehensive database during the development of numerical sediment quality criteria for specific contaminants (Phase II of this study).

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The most common physiological response measured in assessing the toxic effects on benthic invertebrates of the contaminants addressed in this study is survival (see Appendix 2). Other physiological responses measured by specific studies are summarized in Table 2.6.

Other studies involve the detection of behavioural responses of benthic macroinvertebrates to waterborne contaminants. For example, Folmar (1978) reported avoidance by the may fly nymph <u>Ephemerella walkeri</u> of a copper sulphate concentration of 0.1 mg/L. Williams <u>et al.</u> (1987) found that the selection of sites for oviposition by female <u>Chironomus riparius</u> was affected by cadmium. Significantly higher numbers of egg ropes were laid in the control and lower concentrations of cadmium (0.3 and 30 mg/L) than in solutions of 100 and 300 mg/L).

Meyer et al. (1986) reported that dragonfly larvae Libellula depressa, L. quadrimaculata and Aeshna cyanea exposed to 0.020 mg/L of lead for six weeks showed no signs of behavioural disorders in the first two weeks. After four weeks, however, the normal motor activity of the test animals seemed somewhat suppressed. Within the last week of exposure, the food catching activity was profoundly altered, i.e., the organisms were little stimulated by actively moving prev.

Finally, abnormal behaviour generally preceding death has been elicited from benthic invertebrates at high concentrations of toxic chemicals. For example, Spehar et al. (1978) observed that, during sublethal exposure to cadmium, the snail Physa integra was extended from its shell, but was unable to attach the foot or crawl. In addition, abnormal behaviour in the form of a rigorous curling motion and free-swimming was observed for caddisflies Ephemerella sp. exposed to sublethal concentrations of cadmium. In contrast, control larvae were observed in larval cases and responded slowly to probing. Similarly, Anderson and DeFoe (1980) reported that caddisflies Brachycentrus americanus exposed to endrin left their cases and were found lying on the bottom of the test cage, often in a curled configuration. On the other hand, stoneflies, Pteronarcys dorsata, exhibited spontaneous locomotory activity during endrin exposure.

2.1.3.2 Toxicity to Bottom-Dwelling Fish

A substantially larger database is available on the toxicity of contaminants in water to bottom-dwelling fish compared to that for contaminants in sediments. A compilation of

TABLE 2.6: SUMMARY OF PHYSIOLOGICAL RESPONSES OTHER THAN SURVIVAL MEASURED IN TOXICITY STUDIES WITH BENTHIC MACROINVERTEBRATES

Physiological Response	Contaminant	Species	Reference
Growth	Ni	Chironomus riparius	Powlesland and George (1986)
	Cu	Physa integra, Campeloma decisum, Cammarus pseudolimnaeus	Arthur and Leonard (1970)
	Cd, Cu, Pb, Zn	Tanytarsus dissimilis	Anderson et al. (1980)
	Cu	Paratany tarsus par thenogeneticus	Hatakeyama and Yasuno (1981)
	Cd, Cr, Cu, Pb	Biomphalaria glabrata	Ravera (1977)
	Cu, Ni	Hydra littoralis	Santiago-Fandino (1983)
Reproduction	Cd, Cr, Cu, Pb	Biomphalaria glabrata	Ravera (1977)
	Cu, Ni	Clistoronia magnifica	Nebeker et al. (1984c)
	Cu	Paratanytarsus parthenogeneticus	Hatakeyama and Yasuno (1981)
	a-BHC	Lymnaea stagnalis	Canton and Slooff (1977)
	PCB	Gammarus pseudolimnaeus	Nebeker and Puglisi (1974)
	Cu	Chironomus decorus	Kosalwat and Knight (1987a)
Adult Emergence	Cu, Ni, Zn	Clistoronia magnifica	Nebeker <u>et al.</u> (1984c)
	Cu	Paratany tarsus parthenogeneticus	Hatakeyama and Yasuno (1981)
	DDE	Chironomus tentans	Derr and Zabik (1972)
	PCB	Tany tarsus dissimilis	Nebeker and Puglis: (1974)
	Mirex	Chironomus plumosus	Sanders <u>et al.</u> (1981)
	DDT	Acroneuria pacifica, Pteronarcys californica	Jensen and Gaufin (1964b)
Respiration	Cd, Cr, Cu, Hg, Nr, Zn	<u>Tublifex</u> <u>tublifex</u>	Brkovic-Popovic and Popovic (1977b
	Cd, Hg	Limnodrilus hoffmeisteri, Tubifex tubifex	Chapman et al. (1982b)
	Pb	Orconectes virilis	Anderson (1978)
Osmoregulation? Water Balance	Zn	<u>Simulium ornatipes</u>	Carter (1980)
Total Protein Content	Cd	Chironomus tentans	Rathore <u>et al.</u> (1979)
Enzyme Activity	Pb	Libellula depressa, L. quadrimaculata, Aeshna cyanea	Meyer <u>et al.</u> (1986)
Heart Rate	a -BHC	Lymnaea stagnalis	Canton and Slooff (1977)

toxicity data for the contaminants addressed in this study was not undertaken. Comprehensive databases for the toxicity of waterborne contaminants to fish (including bottom-dwelling fish) are provided in numerous summary documents, and can be accessed in Phase II of this study, i.e., during the development of numerical sediment quality criteria for specific contaminants. Table 2.7 lists some of the available summary documents. These documents usually provide comprehensive databases for the toxicity of waterborne contaminants to benthic macroinvertebrates. Table 2.7 also lists other readily available, recent journal articles and reports with relevant toxicity data for bottom-dwelling fish.

The most common physiological responses measured in assessing the toxic effects on bottom-dwelling fish of the contaminants addressed in this study are survival, growth and reproduction (e.g., Henderson et al., 1958; Pickering and Vigor, 1965; Pickering and Henderson, 1966; Mount, 1968; Brungs, 1969; Mount and Stephan, 1969; Grant and Mehrle, 1970; Pickering and Gast, 1972; Stalling and Mayer, 1972; Nebeker et al., 1974; Pickering, 1974; Argyle et al., 1975; Brungs et al., 1976; Mayer et al., 1977; Benoit and Holcombe, 1978; Defoe et al., 1978; McCarty et al., 1978; Blaylock and Frank, 1979; Buckler et al., 1981; Lima et al., 1984; Spehar and Carlson, 1984).

Other physiological responses measured are changes in biochemical composition (e.g., Grant and Mehrle, 1970; Mehrle et al., 1981; Klaverkamp et al., 1983; Bengtsson and Larsson, 1986), enzyme activity (e.g., Kendall, 1975; Bengtsson and Larsson, 1986), thyroid activity (e.g., Mayer et al., 1977), histopathological changes (e.g., Hansen et al., 1976), and gross morphological changes (e.g., Kendall, 1975; Buckler et al., 1981; Mehrle et al., 1981; Bengtsson and Larsson, 1986).

Numerous researchers have documented the ability of fishes to avoid sublethal concentrations of toxic chemicals. Since they are mobile, fish increase their survival potential by exhibiting an avoidance response to deleterious aquatic environments. However, there may be no particular relationship between behavioural responses of a fish to a contaminant and the toxic effects of that contaminant. Furthermore, avoidance has been shown to occur only in response to particular toxic chemicals.

Behavioural studies involving bottom-dwelling fish species include that by Weir and Hine (1970) who used a conditional shock avoidance technique to demonstrate impaired

TABLE 2.7: LIST OF SUMMARY DOCUMENTS WITH COMPREHENSIVE DATABASES AS WELL AS OTHER RECENT REPORTS ON TOXICITY OF WATERBORNE CONTAMINANTS TO BOTTOM-DWELLING FISH

Contaminant	Fish Species ¹	Reference*			
Arsenic	FM CC, FM	Lima <u>et al.</u> (1984) Demayo <u>et al.</u> (1979)*			
Cadmium	C, FM, G, TS, WS CC, FM, G TS FM, G	U.S. EPA (1980a)* Phipps and Holcombe (1985) Eisler (198 <i>5</i> a)* Reeder <u>et al.</u> (197 <i>9</i> a)*			
Chromium	C, FM, G C, FM CC, FM, G, WS	U.S. EPA (1980b)* Taylor <u>et al.</u> (1979a)* Eisler (1986a)*			
Copper	BrB, C, CC, FM, G, WS BrB, C, CC, FM, G, TS, WS BrB, FM, G, WS	U.S. EPA (1980c)* Harrison and Bishop (1984)* Demayo and Taylor (1981)*			
Lead	CC, FM, G, WS	U.S. EPA (1980d)*			
Mercury	C, CC, FM, G, TS, WS CC FM	U.S.EPA (1980e)* Eisler (1987)* Reeder <u>et al.</u> (1979b)			
Nickel	C, CC, FM, G FM	U.S. EPA (1980f)* Taylor <u>et al.</u> (1979b)*			
Zinc	C, FM, G FM	U.S. EPA (1980g)* Taylor and Demayo (1980)*			
Aldrin	BIB, C, CC, FM, G BIB, CC, FM	U.S. EPA (1980h)* Mayer and Ellersieck (1986)*			
α-BHC		U.S. EPA (1980i)*			
γ-ВНС	BIB, C, CC, FM, G BIB, CC, FM, G	U.S. EPA (1980i)*			
Chlordane	C, CC, FM, G CC, FM, WS	U.S. EPA (1980j)* Mayer and Ellersieck (1986)*			
DDD	CC CC, FM	U.S. EPA (1980k)* Mayer and Ellersieck (1986)*			
DDE		U.S. EPA (1980k)*			

TABLE 2.7: LIST OF SUMMARY DOCUMENTS WITH COMPREHENSIVE DATABASES AS WELL AS OTHER RECENT REPORTS ON TOXICITY OF WATERBORNE CONTAMINANTS TO BOTTOM-DWELLING FISH

Contaminant	Fish Species ¹	Reference*
DDT	BIB, C, CC, FM, G BIB, C, CC, FM, G	U.S. EPA (1980k)* Mayer and Ellersieck (1986)*
Dieldrin	BIB, C, CC, FM, G BIB, CC, FM, G	U.S. EPA (1980h)* Mayer and Ellersieck (1986)*
Endrin	BIB, C, CC, FM, G, TS CC, FM, G BIB BIB, C, CC, FM, G	U.S. EPA (19801)* Thurston <u>et al.</u> (1985) Anderson and DeFoe (1980) Mayer and Ellersieck (1986)*
нсв	CC, FM CC, FM	U.S. EPA (1980m)* Mayer and Ellersieck (1986)
Heptachlor	FM, G BIB, CC, FM	U.S. EPA (1980n)* Mayer and Ellersieck (1986)*
Mirex	FM CC, FM FM	Buckler et al. (1981) Eisler (1985b)* Mayer and Ellersieck (1986)*
PCB	C, CC, FM CC CC, LS, WS	U.S. EPA (1980o)* Eisler (1986b)* Mayer and Ellersieck (1986)*

Bottom-dwelling fish species include black bullhead (BIB), brown bullhead (BrB), carp (C), channel caffish (CC), fathead minnow (FM), goldfish (G), longnose sucker (LS), threespine stickleback (TS) and white sucker (WS).

Reference includes database on toxicity of waterborne contaminants to benthic macroinvertebrate species.

performances by goldfish to metal (arsenic, lead, mercury) concentrations below the 1% lethal concentration (LC₁).

Westlake and Kleerekoper (1970) showed that a "memory" or retention process was involved in the turning behaviour of the goldfish. Davy et al. (1972) reported that a highly significant time-dependent correlation between consecutive turns in the locomotor pattern of goldfish was significantly reduced within four days by chronic exposure of the fish to 10 ug/L DDT. This behaviour was attributed to the "memory" process in the pertaining locomotor control mechanism in the central nervous system. Return of the fish to clean water for 130 to 139 days did not result in the restoration of the above correlation.

Kleerekoper (1973) reported that shallow gradients of copper (0.011 to 0.017 mg/L) attracted goldfish, whereas channel catfish (Ictalurus punctatus) were not as strongly attracted. In contrast, white sucker (Catostomus commersoni) had a significant avoidance reaction. When higher copper concentrations (0.025 to 10.0 mg/L) were used, goldfish entries into the copper zone were significantly less frequent (Westlake et al., 1974).

2.1.3.3 Modifying Factors

Experimental results have shown that the concentrations of waterborne contaminants inhibiting growth, reproduction and other physiological processes in benthic macroinvertebrates and bottom-dwelling fish vary considerably, depending on such factors as life stage, physiological state, nutrition, predator-prey interactions, competition, disease and parasitism, substrate, light, temperature, pH, water hardness, dissolved oxygen and other water quality parameters. A summary of some of these modifying factors is presented in Table 2.8. In addition, Buikema and Benfield (1979) have reviewed the effects of some of these factors in modifying the toxicity of contaminants to benthic macroinvertebrates.

As discussed in Section 2.1.2.3, the presence of sediments modifies the toxicity of contaminants (e.g., Chapman et al., 1982a; Nebeker et al., 1986a; Burton et al., 1987). Sorption of the contaminants to the sediments appears to play an important role in the reduction of toxicity.

TABLE 2.8:	SUMMARY OF MODIFYING FACTORS AFFECTING TOXICITY OF WATERBORNE CONTAMINANTS TO BENTHIC
	MACROINVER TERRATES AND ROTTOM DWELLING FISH

Factor	Contaminant	Species	Remarks	Reference
Life Stage	Cd, Cr, Cu, Ni, Zn, 7-BHC, PCB	Pirnephales promelas	Embryo-larval and early juvenile life stages were the most, or among the most, sensitive	McKim (1977)
	Cu	Asellus aquaticus, Proasellus coxalis	Embryonic and larval stages, most sensitive	de Nicola Guidici <u>et al.</u> (198)
	Cd	Asellus aquaticus, Proasellus coxalis	Juveniles more sensitive than adults	de Nicola Guidici <u>et al.</u> (198
	Cu	Chironomus tentans	First-instar larvae most sensitive followed by second-, third- and fourth-instar larvae	Nebeker <u>et al.</u> (1984a)
	Cd	Asellus aquaticus	Smaller juveniles more sensitive than larger juveniles and adults	Green <u>et al.</u> (1986a)
	Cd	Chironomus riparius	Larval tolerance increased with age	Williams <u>et al.</u> (1986)
	Cu, 1-BHC	Gammarus pulex	Size of organism did not influence toxicity	Stephenson (1983)
	DDT	Claasenia sabulosa, Pteronarcella badia	Tolerance greater in larger naiads	Sanders and Cope (1968)
	Cd	Gammarus pulex	Post-molt adults 200 times more sensitive than intermolt adults	Wright and Frain (1981)
	Cu	Chironomus decorus	Eggs most tolerant	Kosalwat and Knight (1987a
Hardness	Cu	Gammarus pulex	Cu 4 to 6 times more toxic in soft water than hard water	Stephenson (1983)
	γ-BHC	Gammarus pulex	LC50 values from 72-hr onwards were significantly higher in soft water than in hard water	Stephenson (1983)
	Cd, Cr, Cu, Hg, Ni, Zn	<u>Tubifex</u> tubifex	Decreased toxicity with increasing hardness	Brkovic-Popovic and Popovi (1977a)
	Cd	Carassius auratus	Decreased toxicity with increasing hardness	McCarty <u>et al.</u> (1978)
	Cd, Cr, Cu, Pb, Nı, Zn	Pimephales promeias	Decreased toxicity with increasing hardness	Pickering and Henderson (1966)
pН	>-BHC	Chironomus riparius	Significantly more toxic at pH 6 than at pH 9 and 8	Warwick Fisher (1985)
	Zn	Pimephales promelas	More toxic at pH 8 than at pH 6	Mount (1966)
Temperature	Cd	Cambarus latimanus	No effect	Thorp et al. (1979)
	Cr, Cu, Zn	Carassius auratus	Increased toxicity with increasing temperature	Smith and Heath (1979)
Species Intermixing	Cd, Hg	Tubifex tubifex/ Limnodrilus hoffmeisteri	Species intermixing decreased toxicity	Chapman <u>et al.</u> (1982b)
Calcium	Cd	Gammarus pulex	Antagonistic effect on cadmium toxicity	Wright and Frain (1981)
Previous Exposure	Fe	Asellus aquaticus	Previous exposure to elevated iron concentrations resulted in greater tolerance	Malthy <u>et al.</u> (1987)
Predator-Prey Interactions	Cd	Pimephales promelas	Increased prey vulnerability	Sullivan <u>et</u> <u>al.</u> (1978)

Spehar and Carlson (1984) reported that acute toxicity tests conducted monthly in St. Louis River water (Duluth, MN) showed that cadmium toxicity to fathead minnow varied by more than a factor of three over the year, indicating the need for considering the effects on toxicity potential of seasonal changes in physical and chemical characteristics of site water.

Furthermore, a number of studies have investigated the effects of synergistic and antagonistic interactions of toxic chemicals on fish. For example, Eaton (1973) reported that a mixture of copper, cadmium and zinc had a synergistic effect on toxicity to the fathead minnow during a 12.5-month chronic test. A lethal threshold was attained in the mixture when each metal was present at a concentration of 0.4 times or less of its individual lethal threshold. Howell (1985) reported that the presence of zinc has an antagonistic effect on cadmium toxicity to the amphipod G. pulex. Other studies with fish have reported additive toxicity for mixtures of arsenic and PCBs; an antagonistic effect of PCB (Aroclor 1254) against cadmium toxicity; and a strong antagonistic effect of selenium against mercury toxicity.

With prolonged exposures, fish may show partial or complete physiological acclimation to chronic concentrations of toxic chemicals. Duncan and Klaverkamp (1983) demonstrated that tolerance and resistance of white suckers (C. commersoni) to cadmium were increased by antecedent metal exposure. White suckers exposed to elevated cadmium, mercury or zinc levels subsequently survived longer in cadmium toxicity tests than control (non-exposed) suckers. A number of mechanisms that might be responsible for the reduced cadmium toxicity were proposed, including decreased uptake, increased excretion, redistribution of metals to less-sensitive target sites, and/or induced synthesis of metallothionein, a protein believed to function in the detoxification and storage of metals.

Fish have been shown to be capable of metabolizing several classes of organic compounds (Lech and Bend, 1980; Binder et al., 1984; Lech and Vodicnik, 1984). Many species of fish possess most of the hepatic enzyme activities that have been demonstrated to exist in higher invertebrates. Based on both in vitro and in vivo experiments, fish are capable of many Phase I (dealkylation, hydrolysis) and Phase II (acetylation, conjugation) biotransformation reactions; however, the rate and pathways for a given compound may vary widely among species of fish. In several instances, it has been demonstrated that

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the rate of biotransformation of certain compounds can be sufficient to have significant effects on chemical toxicity and residue dynamics. For example, Hinz and Matsumura (1977) reported that metabolism of 2,5,2'-trichlorobiphenyl by goldfish approached that of the rat. In contrast, little or no significant metabolic activity was found for the bullhead Ictalurus.

Biotransformation processes may provide a modulation of the blood and tissue concentrations of the organic toxicant, and control its bioaccumulation and persistence (half-life). Biotransformation may be important in protecting fish from the toxic effects of certain organics by converting them to less biologically active forms. On the other hand, evidence is mounting that certain species of fish can metabolize organics, that are less toxic (or non-toxic) to more toxic forms, or that are not carcinogenic to active carcinogenic forms (Lech and Vodicnik, 1984).

2,1,4 Extent of Sediment Genotoxicity Data

2.1.4.1 Background

Genetic responses of aquatic organisms to pollution stresses have received little attention. A number of morphological abnormalities, especially tumors in fish and congenital anomalies in birds, have been documented in some Great Lakes biota. Some of these occurrences may be genetic responses; others may result from non-genetic, developmental problems. The causal agents and mechanisms remain largely unkown.

Mutagenic toxic substances are usually of far greater direct hazard and significance to man than to other biotic populations (Woodwell, 1970). A slightly enhanced rate of mutation due to mutagenic chemicals is significant to man, because of the value placed on the individual in society. In contrast, a slightly increased mutation rate is inconsequential to other biotic populations since most genetic defects are eliminated through natural selection.

A significant number of compounds have been identified as having mutagenic, carcinogenic or teratogenic activity (Huff, 1982; Soderman, 1982a,b). Notwithstanding natural repair of genetic damage, mutations tend to accumulate over the lifetime of a cell. Many heritable mutations result from faulty repair of more serious, non-heritable

genetic damage. Heritable mutations can be passed on to the descendants of a replicating somatic cell, or through the germ cells, to the progeny of a reproducing organism. Since mutations can accumulate in this fashion, an organism's mutational load tends to be proportional to mutagen concentration and exposure over its lifetime.

Both mutagenesis and carcinogenesis have been associated with chromosomal damage. Therefore, it has been hypothesized that the first essential event in malignant transformation is a mutational event. This theory, known as the somatic mutation hypothesis, predicts that mutagens are carcinogens. However, recent studies have shown a significant number of mutagens that are not carcinogens, and a few nonmutagens that are carcinogens. It is generally assumed for regulatory purposes that there is no threshold exposure for the initiation of mutagenic or carcinogenic manifestations (e.g., OSTP, 1984).

Teratogenic agents act during embryonic development to produce physical or functional defects in the fetus or offspring. The defects may result from damage to the genetic material controlling development and many mutagens have such teratogenic effects. However, embryonic development is also subject to non-genetic perturbation, and many strong teratogens do not produce mutations. Response thresholds, or minimum effective dosages, have been demonstrated for some teratogens.

An increasing number of studies have been undertaken in the past ten years to assess the frequency and extent of mutagenic, carcinogenic and teratogenic events among aquatic populations, including those of the Great Lakes. Assay methods applicable to assessment of such hazards associated with polluted sediments are summarized in Table 2.9 and reviewed in the following sections. Other assay results indicating the genetic and teratogenic effects of the specific metals and pesticides which are the subject of this review are summarized in Table 2.10.

2.1.4.2 Mutagenic Assays

A number of biological assays have been developed for assessment of mutagenic potential of environmental media. Of these, the Ames' <u>Salmonella/microsome</u> bacterial reversion test developed by Ames <u>et al.</u> (1975) is the most practical, expeditious and economical for monitoring the incidence of mutagens in the natural environment (e.g., Johnston and

Genotoxic Response/Test	Location	Reference
Ames Test/ Bacillus subtilis rec-assay	Japan Southwestern Lake Michigan Buffalo River, Lake Erie Black River, Lake Erie Hamilton Harbour, Lake Ontario	Kinae et al. (1981a), Suzuki et al. (1982), Sato et al. (1983) Alien et al. (1983) West et al. (1983) Black et al. (1980) Metcalfe (1987)
Tradescantia stamen hair assay	Missouri reservoir	Lower <u>et al.</u> (1985)
Chironomid Deformities	Okanagan Valley lakes, B.C. Qu'Appelle River, Sask. Telkow Kanal, West Germany Swedish lakes Experimental ponds Thunder Bay, Lake Superior Parry Sound, Georgian Bay Lake Erie Central Basin of Lake Erie Port Hope Harbour, L. Ontario Bay of Quinte, Lake Ontario Black River Bay, Lake Ontario Laboratory Exposures	Hamilton and Saether (1971) Warwick (1980b) Koehn and Frank (1980), Frank (1981) Wiederholm (1984) Cushman (1984) Crowther and Luoma (1984) Hare and Carter (1976) Brinkhurst et al. (1968), Hamilton and Saether (1971) Krieger (1984) Cook and Veal (1968), McKee et al. (1985), Warwick et al. (1987) Warwick (1980a) Boc sor et al. (1974) Kosalwat and Knight (1987a), Hart et al. (1986a), Hamilton and Saether (1971)
Plecopteran Deformities	Bow River, Alberta New York State	Donald (1980) Simpson (1980)
Oligochaete Deformities	Swedish lakes British Columbia lakes	Milbrink (1980) Chapman and Brinkhurst (1984), Roch <u>et</u> al. (1985)
Fish Neoplasia	Puget Sound, Washington Final Oxidation Pond, Alabama Torch Lake, Lake Superior Black River, Lake Erie	Malins <u>et al.</u> (1984, 1985a, b) Grizzle and Melius (1983) Black <u>et al.</u> (1982) Baumann <u>et al.</u> (1982), Black <u>et al.</u> (1985)

TABLE 2.9: GENOTOXICITY STUDIES OF SEDIMENTS

Genotoxic Response/Test	Location	Reference
Fish Neoplasia	Buffalo River, Lake Erie Hamilton Harbour, Lake Ontario Welland River	Black et al. (1980, 1981, 1985), Black (1982, 1983) Metcalfe (1987) Dickman and Steele (1986)
Fish/Amphibian Teratogenesis	Laboratory Exposures	Birge <u>et al.</u> (1977)

			Test System ^{2, 3}				Carcinogen	Mammalian		
Chemical	An	Ivt	Ames	Mc	Uds	CIvv	Clvt	Dros	Candidate	Terata ³
Aldrin	М		-				Р		EPA	мн
As	1								EPA, OSHA	
Ca ₂ (AsO ₄) ₂			-						EPA, OSHA	
Na ₂ (AsO ₄) ₂		P	-	N			P		EPA	MH
BHC	M								OSHA	
Cd	R								EPA, OSHA	P
Cd Cl	RM	P	2		-		N	-	EPA, OSHA	
Cd SO ₄	RM						P		EPA, OSHA	н
Chlordane	M		-	P	2				EPA	-
Cr PO ₄	1									
Ca CrO ₄	R	P					P		EPA, OSHA	
Na CrO ₄	1	P							EPA, OSHA	
op-DDE	M		-	P	-		P	2	OSHA	
DDT		-	-	-	-	-	P	2	EPA, OSHA	R
Dieldrin	M			P					EPA, OSHA	MH
Endrin	-		-		-					MH
Heptachlor	34		-		~	+			EPA	
Heptachlor Epox.de	1		-					-		
HCB	74		-						EPA	-
Fe ₂ O ₂	-								OSH A	
Pb (Acetate)	RM	P	-	~	\ \	-	N		OSH 4	
РЬ СО3	1									PН
Pb2 (PO ₄₋₂	R								OSHA	
Mirex	RM		-		-				OSHA	R
N. (Acetate)	1								EPA, OSHA	
Ni CO3	P								EPA	RM
Ni .	R								EPA, OSHA	
PCB	RM.					-	N	-	EPA	M

After Soderman (1982a,b), Shepard (1983),

2 Test Systems:

An - Animal Carcinogenesis (in vivo)

lvt = Cell Transformation (<u>in vitro</u>)

Ames = Ames Test

Mc - Mammalian Cell Point Mutation

Clvv - Cytogenetic Test (in vivo)

Clvt = Cytogenetic Test (in vitro)

Dros = Sex-linked Recessive Lethal Test in Drosophila

³ Response Codes:

- M = Positive in Mouse
- R = Positive in Rat
- H = Positive in Hamster
- 1 : Inconclusive
- P = Positive (without microsomal activation)
 - + = Positive (with microsomal activation)
 - N = Negative (without microsomal activation)
 - = Negative (with microsomal activation)
 - ? : Assay Findings Questionable

Herron, 1979). The results are obtained in three to four days and the test normally uses one to five specially constructed strains of <u>Salmonella typhimurium</u> for the detection of frameshift or base-pair substitution reverse mutation at the histidine locus. The histidine mutants developed by Ames <u>et al.</u> (1975) require histidine in their media, but may be reverted to prototrophy by specific chemical mutagens known to cause such changes. Basically, the Ames' test involves application of the test chemical to agar plates containing the bacteria and a metabolic activation system, a sterile extract of activating enzymes, usually from PCB-induced rat liver (ICPEMC, 1983). In this way, a wide variety of carcinogens requiring metabolic activation by mammalian enzymes can be detected as mutagens in the bacterial system.

Based on the Ames test, a number of municipal and industrial wastewater effluents have been shown to have mutagenic properties, including urban runoff and combined sewer overflow (Spiegel et al., 1984), sewage treatment plant wastewater (Rappaport et al., 1979) and pulp and paper mill effluents (Hoglund et al., 1979; Rapson et al., 1980; Kringstad et al., 1981; Donnini, 1983).

Using a <u>Bacillus subtilis</u> rec-assay (Kada, 1975) as well as the Ames' test, Kinae <u>et al.</u> (1981a) found mutagenic activity in ether extracts of sediments collected in the receiving waters of a Japanese kraft pulp and paper mill discharge. Pyrene, fluoranthene, dehydroabietic acid, 2,4,6-trichlorophenol and 3,4,5,6-tetrachloroguaiacol were identified as mutagenic constituents in the extracts, although a number of heavy metals (Pb, Cd, Zn, Hg, As) were also present in the sediments. Significant (p < 0.001) <u>Salmonella reversion frequencies exceeding control levels by up to four times were obtained.</u>

Suzuki et al. (1982) compared the upper (rural) and lower (urban) zones of the Tama River in Japan, with respect to mutagenic activity of sediments, based on the Ames assay. Aqueous extracts were used, thus ruling out polycyclic aromatic hydrocarbons as causative agents, and implicating polar compounds. The response to the neutral fraction was greater in the urban than the rural zone (63.6 vs. 8.0 times control), while the response to the base fraction was greater in the rural than the urban zone (21.6 vs. 8.0 times control). Thus, very different primary active agents were suggested in rural as compared to urban areas.

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Sato et al. (1983) found mutagenic activity in ether extracts of sediments from the Nagara River system in Japan, using the Ames assay. Maximum activity on the Arata River (2.5 times control levels) was found in the neutral fraction of the extract, with microsomal activation. Suspected active agents in this sample were benzo(b-fluoranthene (2.5 ppm), benzo(a)pyrene (1.6 ppm), fluoranthene (0.2 ppm), chrysene (0.5 ppm) and perylene (0.1 ppm). However, maximum activity on the Sakai River (2.8 times control) was found without microsomal activation, also in the neutral fraction. Thus, unknown contaminants, other than polycyclic aromatic hydrocarbons (which require microsomal activation), were implicated.

Allen et al. (1983) undertook a study to identify the presence of mutagenic activity in sediments from both harbour and beach areas of the southwestern shoreline of Lake Michigan near Chicago. Based on the Ames test, the sediments from a number of areas were shown to contain significant levels of mutagenic activity. Maximum sample/control reversion ratios were found at Jackson Park Beach (25.0), Jeorse Park (18.9), Calumet Harbour (13.0), Indiana Harbour (13.0) and Calumet Beach (5.9). A sample/control ratio of 3.5 was considered to be significant.

West et al. (1985, 1986) isolated several fractions from Black River sediments, respectively containing the polycyclic aromatic hydrocarbons (PAHs) and the polycyclic aromatic nitrogen heterocycles (PANH's), for mutagenicity testing. These fractions were tested using the Ames assay, as well as unscheduled DNA synthesis (UDS) in cultured rat hepatocytes. The UDS response reflects genetic repair activity following genetic damage. The PAH fraction elicited the greatest response in the Ames test, while the PANH fraction elicited the greatest UDS response. The latter was 31.7 times the control response level.

Lower et al. (1985) used the <u>Tradescantia</u> stamen hair assay to examine mutagenicity of whole sediments from the bottom of a Missouri reservoir. The stamen hairs of this vascular plant consist of a linear series of unpigmented cells. Somatic mutations at a colour locus produce pink sectors which can be counted to reflect mutation frequency. Plants grown in potted sediment showed mutation frequencies 1.5 times those of control plants grown in clean soil. This elevated mutation frequency was achieved during the first few days of exposure and remained essentially constant over a 91-day study period.

Genetic assays based on sister chromatid exchange (SCE) have been developed for marine benthic organisms. The rate of genetic exchange between the sister chromatids of each chromosome is known to increase in response to mutagenic agents. Pesch et al. (1981) have verified this technique for polychaete worms (Neanthes), and Dixon and Prosser (1986) have extended it to mussel (Mytilus edulis) larvae. However, the timing between chromatid labelling (with BrdU) and cell preparation for scoring is critical and must be determined for each new organism. The technique has yet to be applied to freshwater benthos or bottom—dwelling fish, or to evaluation of sediment samples.

A sex-linked lethal mutation assay has been developed by Samoiloff et al. (1983) using the free-living nematode, <u>Panagrellus redivivus</u>. Mutations can be detected at over 300 essential loci on the x-chromosome, in response to specific toxicants or sediment extracts. The test spans two generations and can be completed in 11 days. A four-day test for inhibition of gene activation during development apparently correlates well with the mutation assay.

2.1.4.3 Fish Neoplasia

Relative to Water Pollution - A General Review

A number of investigators have reported the occurrence of neoplasia in marine and freshwater fish. In a study based on the examination of approximately 290,000 fishes that comprised 151 species collected from southern California coastal waters between 1969 and 1976, Mearns and Sherwood (1974, 1977) reported that approximately 5% of the fishes were affected with external signs of disease, such as fin erosion, tumours, colour anomalies and attached macroparasites. The distribution and frequency of tumour diseases could not be related to direct sources of pollution.

In contrast, Kinae et al. (1981b) reported that the incidence of skin melanoma in the spotted sea trout Nibea mitsukurii was 47.4% at Shinguu, Japan, impacted by pulp and paper mill effluents, whereas melanoma frequency was much lower in uncontaminated areas, i.e., 1.3 and 3.9%, respectively, for Ooigawa and Tagonoura. McCain et al. (1977) reported an overall mean frequency of 32% for hepatomas in English sole Parophrys vetulus from the polluted Duwamish River estuary in Seattle, Washington. Murchelano and Wolke (1985) found cholangio carcinomas and hepato carcinomas in 16 of 200 winter flounder Pseudopleuronestes americanus from Boston Harbor.

Slooff (1983a) reported that among 4,184 fish examined from the Rhine River and its branches, five bream Abramis brama showed liver neoplasia, and two roach Rutilus rutilus exhibited thyroid tumours. For the Mense River, one bream showed a liver neoplasm of 1,435 fish examined. No tumours were found in 714 fish examined from Lake Ijssel, nor in 1,404 fish from the relatively clean Lake Braassem (used as 'control').

Grizzle and Melius (1983) reported a 70% prevalence of oral papillomas in black bullheads (Ictalurus melas) in a final oxidation pond of the Tuskegee, Alabama, sewage treatment plant. Ames' testing of a pond-water concentrate showed mutagenic activity. Based on the negative results of electron microscopy and cell-free tumour homogenate injection studies, virus involvement was not suspected. The lesions persisted in fish removed from the pond and maintained in clean water.

In their study relating increased skin melanoma frequency in spotted sea trout collected from an area impacted by pulp and paper mill effluents, Kinae et al. (1981b) reported that ether extracts of the liver of fish bearing melanoma were the only ones which showed a clear positive DNA-damaging potency based on the Bacillus subtilus rec-assay. Similarly, Osborne et al. (1982) reported increased mutagenic activity based on the Ames' test of tissue extracts from long-nosed dace Rhinichthys cataractae collected from a chlorinated sewage discharge plume in the Sheep River, Alberta.

Sonstegard (1977) reported recent incidences of gonadal tumours in goldfish, carp (Cyprinus carpio) and goldfish x carp hybrids from all four of the Great Lakes bordering Canada. A museum collection of 38 hybrids captured in 1952 off the mouth of the Rouge River at Detroit did not have tumours, while hybrids collected from the same site in 1977 had tumour frequencies as high as 100% in older males. These findings suggest that the levels of mutagenic and/or carcinogenic agents may have increased since the early 1950's. Moreover, 26 hybrids from the Kincardine area of Lake Huron (the least polluted area where hybrids were captured) had an overall tumour frequency of 61%. It was concluded that, because of the widespread distribution of the disease, the causal agent(s) is ubiquitous (e.g., PCBs and/or DDT).

Dickman and Steele (1986) found that, at a site on the Welland River 3 km downstream from Welland, Ontario, carp x goldfish hybrids had a gonadal tumour frequency of 48%. At a site 10 km downstream, the neoplasm rate in hybrids was only 12%. Furthermore,

the age at which gonadal neoplasms first occurred increased from four years at the 3 km site to eight years at the 10 km site. Hybrids collected upstream of Welland had no neoplasms.

Sonstegard (1977) reported widespread occurrence of papillomas in white suckers from all four of the Canadian Great Lakes and the St. Lawrence River. In the upper Great Lakes, overall papilloma frequency ranged from 0 to 0.7%. However, in Burlington Harbour on Lake Ontario, a 29.6% overall tumour frequency was found. In a subsequent study, no tumours were detected in collections made at Dufferin Creek, Toronto, whereas overall tumour frequencies of 2.2, 50.8, 35.1, 8.0 and 0.8% were recorded in Toronto Harbour, Oakville Creek, Burlington Harbour, Jordan Harbour and Rochester, respectively. Studies also indicated that the frequency of tumour occurrence decreased dramatically with increasing distance from the Oakville-Burlington area of Lake Ontario.

Brown et al. (1973) reported that, during the study period of 1967 to 1972, fish populating the polluted Fox River draining into Green Bay had a higher frequency of tumours (4,38%) than the same species of fish in non-polluted Lake of the Woods in northwestern Ontario (1,03%). These findings suggested that, as water pollution increases, there is a corresponding rise in neoplasia in the fish population. Neoplasia included sarcoma, lymphosarcoma, heptatoma, osteogenic papilloma, epithelioma, hepatocarcinoma, epidermoid carcinoma, anal carcinoma, osteoma, neurilemmoma and melanoma. The type of neoplasm manifested generally depended on the species of fish. Many fish presented two distinct types of tumours at different anatomical sites, e.g., an epidermoid carcinoma of the rectum and a different tumour on the fins.

Baumann et al. (1982) reported that two-year-old brown bullhead (Ictalurus nebulosus) from the Black River at Lorain, Ohio had a liver tumour rate of 1.2%, while those three years and older had a 33% rate. In the older group, the skin and lip tumour rates were 14 and 23%, respectively (Baumann, 1984b). In contrast, none of the brown bullhead (sample size of 249 two-year-old and 80 three-year-old) from a control waterbody, Buckeye Lake, had visually observable hepatomas. These rates of tumour incidence can be compared with those found by Brown et al. (1973) for brown bullhead in the polluted Fox River and in the unpolluted Lake of the Woods of 12.2% and 1.98%, respectively.

The high tumour rate for bullheads in the Black River correlated with their high body burden of PAHs. It was concluded that, since the Black River differed from the control site principally in the levels of PAH contamination, this contamination was most likely the causal factor for the elevated hepatoma rate in resident brown bullhead populations.

Baumann (1984b) reported that spring collections of the 1978 year class of brown bullhead in the Black River showed an increase in liver tumour frequency from 1.2% in 1980 to 9.8% in 1981 and 36.9% in 1982. Moreover, much of the increase from the spring of 1981 to the spring of 1982 occurred during the summer, since a late summer collection in 1981 showed that the liver tumour frequency for the 1978 year class had already reached 31.7%. These data demonstrated that tumour initiation and growth are positively correlated with metabolic rate and/or greater bioavailability of the organic carcinogens during periods of higher temperature.

Black et al. (1982) reported that two closely related species of fish, walleye (Stizostedion vitreum) and sauger (S. canadense), from Torch Lake on the Keweenaw Peninsula of Lake Superior exhibited epizootic neoplasms of several types, including hepatocellular carcinomas, dermal ossifying fibromas, and perivisceral masses resembling mesotheliomas that were usually associated with the mesenteric capsule of the spleen. All saugers examined were affected with liver neoplasms. Torch Lake has been used as a repository of copper mining wastes such that about 20% of the original lake volume has been filled in. Black et al. (1982) reported that there was no documented evidence that copper is carcinogenic intrinsically. However, copper ores may contain metals, such as selenium and arsenic, that are considered carcinogenic, or copper or other metals may be acting to catalyze the formation of a compound that is carcinogenic to fishes, e.g., metal-catalyzed formation of carcinogenic nitrosamines from secondary amine compounds contained in domestic sewage effluents discharged to the lake, or perhaps from naturally occurring amines. It was concluded that although the tumours in the Torch Lake fish appear to be circumstantially related to the presence of copper mining wastes, additional study is required to specifically identify the causal factor(s).

In the mid-1970's, a number of studies were undertaken to document the distribution, frequency and causes of hyperplasia and neoplasia in Great Lakes fish populations. Numerous investigations have indicated an association between pollution of the aquatic environment and increased tumour frequencies. These have been recently reviewed by Baumann (1984a) and Black (1984a).

The hyperplastic condition (goiters) found in coho (Oncorhynchus kisutch) and chinook (O. tshawytscha) salmon is undoubtedly due in part to the low availability of iodide in the Great Lakes Basin. However, the involvement of environmental goitrogens, possibly toxic chemicals, is strongly suggested in the etiology of the thyroid disorders.

Sonstegrad and Leatherland (1976) reported that, in a pilot study of Lake Ontario coho salmon in October 1974, nine of 21 fish captured during their spawning run in the Credit River exhibited distinct growths (goiters) on the gill arches, and all had indications of thyroid hyperplasia as evidenced by diffuse swellings at the base of the gill arches. There was a concomitant, significant decrease in serum thyroxine and trilodothyronia values between September and October. All of these manifestations indicate severe hypothyroidism, i.e., increasing need for thyroid hormone during this period but an inability to produce the hormone in sufficient quantities.

Moccia et al. (1977, 1981) reported that coho salmon collected during the 1976 spawning runs from Lake Michigan, Ontario and Erie had overt goiter frequencies of 6.3, 47.6 and 79.5%, respectively. If low iodide availability was the sole factor contributing to goiter development, then an inverse relationship between goiter frequency and lake iodide concentration could be expected. Iodide concentrations in Lake Michigan waters (0.9 ug/L) were only one-half that of Lake Erie (1.7 ug/L) and one-third that of Lake Ontario (2.9 ug/L). In contrast, overt goiter frequencies in Lake Ontario and Lake Erie coho salmon were 7.6 and 12.6 times, respectively, that in Lake Michigan.

Based on the above observations, Moccia et al. (1977) and Leatherland and Sonstegard (1978) proposed that extrinsic environmental conditions may enhance the development of goiters in the low iodide environment. They reported that organochlorine compounds, such as PCBs and mirex, have been shown to alter thyroid activity in coho salmon, resulting in decreased hormone secretions in an already hypothyroid fish. The onset of goiters in coho salmon coincides with the cessation of feeding during spawning migration, and is concomitant with rapid mobilization of lipid deposits. They concluded that the release of stored PCBs and other organochlorine compounds could stress an already depleted thyroid gland, resulting in goiter development. The thyroid hyperplasia, a possible precursor stage of carcinoma, may readily progress to neoplasia, particularly in the presence of carcinogens.

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Moccia et al. (1981) further substantiated the hypothesis that environmental factors are involved in the etiology of goiters in coho salmon, as well as chinook salmon, in the Great Lakes. Both species responded in a similar relative fashion, i.e., both coho and chinook salmon in Lake Michigan were less severely affected than were their Lake Ontario counterparts. Goiters in the majority of herring gulls (Larus argentatus) collected between 1974 and 1984 from the Great Lakes Basin also supports a forage fish-borne goitrogenic etiology (Moccia et al., 1986).

Although direct proof of a causal role for toxic contaminants in presently lacking for the development of tumours in indigenous fish, the toxic chemical causal agents hypothesis is supported indirectly by laboratory experiments, which indicate that a number of chemical carcinogens readily cause tumours in fish. For example, Brown et al. (1975) exposed bluegill and yellow perch over a six-month period to high concentrations of contaminants, e.g., cufferon (0.2 mg/L), cadmium (5 mg/L), magnesium (200 mg/L), sulphate (200 mg/L), benz(a)anthracene (1 mg/L), zinc (5 mg/L), arsenic (5 mg/L), calcium (200 mg/L). Magnesium at 200 mg/L was chronically toxic. In the experimental exposures, 17% of the fish developed epidermoid carcinomas. Magnesium levels in certain portions of the Fox River were shown to approach this high concentration, although the mean was 63.7 mg/L and, therefore, may be a factor in the high tumour frequency of endemic fish. Since magnesium has been shown to produce a loss of specificity of the DNA during helix formation causing mutations to take place, it was theorized that magnesium could be a direct carcinogenic agent.

In a subsequent laboratory study, Brown et al. (1985) exposed goldfish and guppy (<u>Lebistes reticulatus</u>) to waters simulating the Fox River and Lake of the Woods. After a six-week exposure to Fox River water, the fish showed large increases in their leucocyte counts compared to those in the non-polluted water. Moreover, histological examination of test animals of a nine-week exposure to the polluted water showed lymphoreticular neoplasms, similar to the reticular cell sarcoma found in northern pike (<u>Esox lucius</u>) endemic to the Fox River.

Black (1984a) reviewed case histories of neoplasia in eight species of fish from the Great Lakes with respect to environmental pollution and/or known classes of environmental carcinogens present in the aquatic environment. Although several of the neoplasms in feral fish appear to be causally induced by chemicals, on the basis of epizootiology in

relation to known or suspected environmental pollutants, there is direct evidence only in the case of brown bullhead (Black, 1982, 1983).

Relative to Sediment Genotoxicity

The scientific literature presently contains voluminous information, documenting observations of a wide variety of tumours in several species of fish collected from both polluted and non-polluted waterbodies. Several reviews have been written which attempted to relate disease in fish, specifically increased rates of neoplastic or tumourous diseases, to chemical pollution in water (Stitch et al., 1976, 1977; Brown et al., 1977; Mearns and Sherwood, 1977; Sherwood and Mearns, 1977; Sonstegard, 1977; Sindermann, 1979; Black, 1984b; Malins et al., 1984, 1987b; Baumann and Harshbarger, 1985; Mix, 1986). Some of these have been reviewed in the previous subsection.

In contrast, there is a paucity of information which deals directly with the carcinogenic activity of toxic contaminants directly in the sediments, and tumour induction in fish exposed to those sediments. In most cases, the reports of higher than normal tumour prevalences are correlated with water where there is unquestionable contamination by a wide array of chemical pollutants; however, few (if any) causal links have been established to unequivocally link these two observations.

In the last few years, there has been a focus of research activity aimed at elucidating the role of toxic sediments in neoplastic diseases in certain species of bottom-dwelling fish, such as the white sucker, brown bullhead, common carp, goldfish, carp x goldfish hybrids in fresh water, as well as marine fish species, e.g., the English sole, in salt water. The English sole data (Malins et al., 1987a) establish a convincing link between PAHs in sediments and liver neoplasia.

The ability of some bottom-feeding fish to tolerate low concentrations of dissolved oxygen and chronic concentrations of pollutants enables these species to inhabit environments contaminated with toxic chemicals. This physiological tolerance may result in exposure to carcinogenic agents through various routes. These may include direct contact through feeding in contaminated sediment, ingestion in the diet via contaminated detritus and/or food chain organisms, and by absorption through the gills and skin.

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For example, Sonstegard (1977) reported that as the incidence of neoplasms increased in white suckers with increased proximity to toxic pollution, there was a corresponding shift of the epidermal (oral) papillomas from a generalized body distribution to one of exclusive occurrence on or about the lips. It was postulated that these neoplasms were a likely response of the fish to carcinogenic agents encountered in the sediments during the act of feeding.

Black (1982, 1983) exposed brown bullheads in the laboratory to weekly applications to Buffalo River sediment extract (RSE) over a period of 18 months. During the first 12 months, bullheads exposed to the RSE underwent a series of localized skin changes, consisting of skin blanching and coarsening with subsequent development of occasional small hyperplasia. Between 12 and 18 months, progressive changes in the skin occurred, characterized by marked hyperplasia and the occurrence of small papillomas. This induction of epidermal hyperplasia and papillomas as a result of repeated experimental exposure to the PAH-containing Buffalo River sediment extract provides initial experimental evidence linking tumour occurrence in brown bullhead to carcinogenic chemicals in the aquatic environment.

Black et al. (1980) reported that a high percentage of tissue lesions occurred in a fish population sampled from the Buffalo River draining into easternmost Lake Erie. About 35% of the goldfish and carp hybrids carried abnormal appearing gonads, whereas 20 to 25% of the sheepshead Aplodinotus grunniens were affected with dermal lesions. In addition, lip papillomas were observed in a few white suckers, whereas two of nine brown bullhead displayed dermal tumors. One of these tumour growths was highly malignant and had invaded from the dorsum of the upper jaw through the palate. Based on Ames' testing, a strong source of mutagenic activity was located in the river adjacent to the wastewater outflow of a local dye industry. Peak concentrations of PAHs were found at this site. It was also suspected that aromatic compounds with basic characteristics (e.g., anilline dyes) were involved. It was concluded that while the evidence was circumstantial, chronic exposure to a complex mixture of PAHs probably caused several species of bottom-feeding fish to develop neoplasia (Black et al., 1981).

In a following study, mutagenic aromatic amines, including the suspect carcinogen I-naphthylamine, were identified in addition to the PAHs in the sediments and biota of the Buffalo River (Black, 1982). PAHs are widely recognized skin carcinogens in humans and laboratory animals, whereas aromatic amines usually produce liver and bladder tumours.

A major four-year multidisciplinary study was conducted on the relationships between pollutants and diseases of fish in Puget Sound, Washington (Malins et al., 1984). Sediments and fish were analyzed for 26 aromatic hydrocarbons, 12 chlorinated pesticides, eight PCBs, six other chlorinated organic compounds, and 37 metals and other elements. Individuals of three fish species, English sole, rock sole Lepidopsetta bilineata and Pacific staghorn sculpin Leptocottus armatus, were examined for pathological conditions. English sole from the Duwamish Waterway in Seattle and Everett Harbor had the highest prevalences of hepatic neoplasms (16 and 12%, respectively). neoplasm prevalences ranged from 0.5 to 5.5% in other sampling areas within Elliot Bay (Seattle), Commencement Bay (Tacoma) and Sinclair Inlet (Bremerton), neoplasms were also found in rock sole from all the urban embayments at prevalences from 0.7 to 4.8%, with highs of 4.8% in Everett Harbor and 2.5% in the Hylebos Waterway (Tacoma). Staghorn sculpin with hepatic neoplasms were found only in Commencement Bay (prevalences of 1.0 and 1.7%). In the 1979 to 1982 study, hepatic neoplasms were not observed in fish from nonurban areas. However, in a study completed in 1983, English sole with hepatic neoplasms (6.7%) were captured in Port Madison. Other major types of liver lesions were found primarily in fish from the urban embayments. Positive correlations were consistently found between the prevalences of hepatic neoplasms and other hepatic lesion types in English sole and sculpin and the total concentrations of aromatic hydrocarbons. These results are consistent with those obtained from laboratory studies with animals exposed to benzo(a)pyrene. correlations were not found with chlorinated hydrocarbons. Positive correlations were also obtained between metals and liver neoplasia in rock sole. Direct carcinogenic effect of metals is a possibility; however, indirect effects are also likely, including metalinduced disease resulting from changes in levels of "reductants" such as ascorbic acid or reduced glutathione which provide a defense against carcinogenic electrophiles.

Recently, Malins et al. (1987a) and Willford et al. (1987) have published significant data showing that organic chemicals in sediments are bioavailable to bottom-dwelling fish. The English sole had stomach contents with concentrations of a number of aromatic hydrocarbons (AHs) similar to those in sediments from where the fish were collected, as well as high prevalences of liver neoplasms (Malins et al., 1987a). Xenobiotic metabolites of these AHs were also found in the bile of these fish, and the concentrations of these metabolites were also correlated with the occurrence of liver tumours. These author's reported that the greatest number of lesions of all types in fish from these same

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waters were found in the liver, kidney and gills, suggesting that these may be the primary target organs for genotoxic effects of sediment contaminants.

Although the evidence is somewhat circumstantial, the data strongly suggest that AHs in the sediments are transfered to the English sole via the food chain, and are responsible for liver tumour induction in this species in Puget Sound. This is one of the few studies which provides a well-documented and believable link between fish neoplasia and sediment contamination.

Black (1984) exposed brown bullheads to river sediment extract administered in the diet for 12 months and noted liver lesions in two of six fish which were similar to Type A hepatocellular neoplasms in rodents. This suggests that liver carcinogens are present in the sediments, and may be related to neoplasm development in some Great Lakes fish species. Owing to the fact that the liver is a sensitive, primary target organ for toxic chemical effects, Black (1984) suggests that epizootic liver neoplasia in any wild fish population is a relevant indication of chemical carcinogens in the environment. This may be a highly overstated implication to the finding of liver tumours in wild fish.

As discussed previously, sediment samples derived from kraft paper mills were shown to have extractable fractions which exhibited strongly mutagenic activity using bacterial tests (Kinae et al., 1981a). At least 28 different organic compounds were identified in these sediments, some of which have been shown to experimentally induce liver tumours in fish. Spotted sea trout (a bottom-dwelling fish) collected from these same areas had livers which contained several of these same 28 compounds, and which also produced mutagenic activity (Kinae et al., 1981b). In addition, these fish had an elevated prevalence of skin melanoma. These data suggest that mutagenic compounds in the sediments may be transferred to indigenous fish where they are concentrated in the liver and maintain their mutagenicity, and are potentially linked to tumour occurrence in these fish.

Baumann and Harshbarger (1985) reported an elevated prevalence of liver tumours in brown bullheads in the Black River which they believe to be chemically-induced, and the result of polynuclear aromatic hydrocarbon which most likely originated from a sediment reservoir.

Finally, Malins and Roubal (1985) reported the occurrence of free radicals derived from nitrogen-containing xenobiotics in both sediments and bottom-dwelling fish from Eagle Harbor, Puget Sound. In addition, these same sediments contained high concentrations of aromatic hydrocarbons. These data combine to support an etiologic mechanism to explain the occurrence of hepatic neoplasms and other lesions in English sole taken from these waters.

Mix (1986) recently published a critical review of the literature related to neoplasms in aquatic animals and their association with environmental contaminants. In his paper, Mix challenges the scientific credibility of many of the papers discussed in this current report, and questions the objectivity of researchers who speculate on the causal rate of sediment toxicity to tumour induction when only highly equivocal data and poorly controlled experiments are presented. In most cases, the critism is valid, and exposes the major limitations of the many epidemiological studies which have been conducted on fish.

In summary, it would appear that there is much circumstantial, but also some strong, scientific evidence to support the hypothesis that contaminant-laden sediments may be related to tumour induction in fish, particularly in bottom-dwelling species which live in continuous, close proximity to these sediments. Of all the tumours reported herein, the liver seems to be a primary target for neoplastic changes resulting from toxic-sediment exposure, and epizootics of liver tumours may be a useful indicator of rapid degradation of sediment quality.

Aside from relatively crude approaches to exposing fish to sediment contaminants (either via extracts applied to the water, feed or directly to the fish), there are no other useful models with which to measure the whole-animal response to sediment genotoxicity.

In spite of the equivocal nature of the research produced to date, there is clearly a logical relationship which must exist between contaminated sediments and tumour occurrence in bottom-dwelling fish. Further research is, therefore, essential to develop the appropriate models and field techniques to establish this cause-effect relationship, and to permit ongoing assessment of the biohazards of in situ sediment contaminants.

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2.1.4.4 Teratogenic Responses

Terata have frequently been reported in sediment-dwelling organisms, usually in association with known or suspected sediment pollution, and often in chironomid larvae. However, it is not known whether these have a genetic basis, and specific causal agents have seldom been identified.

Hamilton and Saether (1971) found deformed specimens of four genera of chironomid larvae, Protanypus, Chironomus and <a href="Stitotochironomus in samples collected from two lakes in the Okanagan Valley of British Columbia. The deformed larvae had severely aberrant mouthparts and the head capsules were usually heavily pigmented. In most cases, both the head capsule and body wall were many times thicker than in normal specimens. The deformed specimens were generally found near known sources of pollution. Samples taken nearer the source charactistically contained no specimens of the species.

Preliminary laboratory experiments were undertaken involving exposure of Chironomus tentans culture to aldrin, DDE, 2,4-D, 2,4,5-T, nitrilotriacetic acid (NTA), or PCBs (Hamilton and Saether, 1971). In all cases, excepting the NTA exposure, the culture was either eliminated or drastically reduced with the higher concentration of each of the chemicals. Populations subjected to the lower concentrations were never eliminated although, in some cases, considerable mortality did occur. A small proportion (<10%) of the larvae exposed to 10 ug/L of DDE were found to be deformed with thickened body walls. Possible abrasion of teeth and mandibles by the sandy substrate used for rearing may have obscured mouthpart effects in these experiments (Warwick, 1980b). However, Hart et al. (1986b) recently demonstrated that deformed mouthparts similar to those seen in chironomids from polluted environments can be induced by a genotoxicant (ethyl methane sulfonate) in the laboratory. Similarly, Kosalwat and Knight (1987a) induced mouthpart deformities in C. decorus by spiking food and substrate with copper.

Warwick (1980b) reported that 2.26% of the <u>Chironomus</u> spp. larvae collected from the western basin of Pasqua Lake had deformed mouthparts, whereas 3,13% of <u>Paratendipes</u> sp. larvae in the eastern basin were deformed. Abnormal thickening of the head capsule and body walls, described by Hamilton and Saether (1971), was not evident. Unusually high concentrations of heavy metals as well as the presence of organochlorine pesticides have been monitored in the Qu' Appelle River immediately above Pasqua Lake.

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Koehn and Frank (1980) found high frequencies of aberrations of the labial plates of Chironomus thummi ranging from 25.4 to 37.6% at five stations in the Telkow Kanal in West Berlin. Moreover, Frank (1981) reported that, in the most polluted areas of this channel, 20% of the C. riparius collected showed deformities of the mentum, as did C. plumosus, which became dominant in the less polluted areas. The Telkow Kanal is polluted with high levels of cadmium, copper, lead and zinc.

Wiederholm (1984) reported that the occurrence of deformed mouthparts in recent and subfossil material of mostly Chironomus, Micropsectra and Tanytarsus from Swedish lakes increased from less than 1% of the larvae at unpolluted sites or time periods to values in the range of 5 to 25% at strongly polluted sites. The highest frequencies in Chironomus corresponded with maximum contamination factors for nickel, lead, chromium and zinc. Other metals present included copper, cadmium and mercury at lower levels of contamination.

Larval \underline{C} , decorus taken from experimental ponds to which a coal liquid had been added were found to have deformities of the mentum (Cushman, 1984). The percent occurrence of 'all deformities' (involving both medial and lateral teeth) ranged from 2.7 to 4.6%, and was independent of dose, although the highest frequency was observed at the high dose. However, aberrations of the medial portion of the mentum were significantly dose-related, with a maximum frequency of 1.9% at the highest treatment level (375 mL/m^3). The experimental results may have been confounded by the effects of adult migration from pond to pond.

Warwick (1985) presented an indexing scheme for classifying antennal deformations in Chironomus to illustrate the potential for using deformities in chironomid larvae as a biological screening technique for the detection and assessment of contaminants in aquatic ecosystems. However, mouthparts are easier to prepare for scoring.

Brinkhurst et al. (1968) and Hamilton and Saether (1971) reported that all three specimens of <u>Chironomus</u> spp. collected at stations in the western end of Lake Erie near the mouth of the Maumee River were badly deformed. The most conspicuous feature of these larvae was an exceedingly thick exoskeleton. The head capsules were also thickened and heavily pigmented, and the mouth parts exhibited a variety of aberrations. Stations from the remainder of the lake yielded more than 1,700 specimens, all of which appeared normal. The Maumee River receives a heavy industrial chemical input.

Warwick (1980a) recovered a number of deformed chironomid larvae, with similar characteristics to those described by Brinkhurst et al. (1968), from core sediments collected in the Bay of Quinte, Lake Ontario. The deformed larvae were characterized by twisted, gnarled, asymmetrical teeth in the mentum and mandibles, as well as a thickened cuticle of the body and head capsule walls. The percentage of deformed specimens of Chironomus and Procladius clearly increased in the most recent sediments. Based on sediment core dating, the incidence of deformities increased from 0.09% in the pre-European sediments to 1.06% at 4.5 cm (1951) and 1.99% in the 1972 chironomid population.

Cook and Veal (1968) noted that most <u>Chironomus</u> at a station near an industrial discharge in the turning basin of Port Hope Harbour, Lake Ontario, had deformed labial plates. McKee <u>et al.</u> (1983) and Warwick <u>et al.</u> (1987) reported a deformity frequency of 83% for <u>Chironomus</u> specimens collected in the turning basin compared with only 14% in the outer harbour. Sediment quality data showed that the harbour is heavily contaminated by U-238 decay chain radionculides and several trace metals, particularly in the turning basin, while the outer harbour was relatively uncontaminated. Provincial dredge spoil disposal guidelines were exceeded in the inner harbour by Pb, Ni, Cr, Fe and Cu. Radiation dose rates to larvae were estimated from radionuclide concentrations at 1 mGy/day. The difference in frequencies of deformed larvae from the inner and outer harbour areas suggests that deformities are related to the areal extent of contamination.

Bocsor et al. (1974) reported the occurrence of large proportions of deformed <u>Chironomus</u> in Black River Bay, Lake Ontario, and implicated pollution by agricultural and industrial toxicants. Frequencies of deformed labial plates ranged from 17 to 59%. Crowther and Luoma (1984) reported absence of chironomids near pulp and paper mill discharges in Thunder Bay, Lake Superior, and deformed larvae of the species <u>C. selanarius</u> decreasing in frequency with distance from the outfall.

In the central basin of Lake Erie, Krieger (1984) reported that one specimen of Chironomus near the mouth of the Grand River at Fairport Harbor, and two specimens of Procladius near the mouths of the Black River at Lorain and the Cuyahoga River at Cleveland possessed deformed labial plates or ligulae. It was concluded that further investigation of the incidence and nature of these deformities is required before ascribing them to anthropogenic causes, since the three specimens were widely dispersed and one was taken near the Lorain municipal water intake.

In Parry Sound Harbour, Georgian Bay, Hare and Carter (1976) found a high proportion (77%) of <u>Chironomus</u> (s.s.)? <u>cucini</u> larvae with deformities of the mouthparts. The harbour has been heavily polluted over the past century by explosives, smelting, petroleum and lumber industries, as well as urban sewage discharge, and was the site of a massive oil spill in the 1950's. Of 73 larvae examined from outside Parry Sound Harbour, only one specimen, from Depot Harbour, was found to be slightly deformed. In and near Parry Sound Harbour, single deformed specimens of <u>Procladius</u> sp. and <u>Micropsectra</u> sp. praecox group were also collected.

Morphological deformities have been reported for other benthic invertebrate taxa. For example, Donald (1980) reported deformities of the antennae, maxilla, labium and cerci of two species of Plecoptera, <u>Isocapnia integra</u> and <u>Utacapnia columbiana</u> collected downstream of domestic sewage and industrial outfalls discharging to the Bow River in Alberta. Maximum deformity frequencies for these species were 80% and 14% respectively, as compared to 0% and 3% for controls from pristine sites. Simpson (1980) reported reduced tracheal gills in Plecoptera, <u>Phesganophora capitata</u>, and Trichoptera, <u>Cheumatopsyche</u> sp., downstream of a sewage treatment plant on Gooseberry Creek, New York. Three of three, and ten of 12 larvae, respectively, were abnormal. This effect was attributed to chlorine or halogenated compounds.

Milbrink (1980) reported that the oligochaete <u>Potamothrix hammoniensis</u> exposed to high sediment mercury levels exhibited setal abnormalities. Chapman and Brinkhurst (1984) and Roch <u>et al.</u> (1985) also noted setal abnormalities, with enlarged and distorted dorsal pectinate setae, in oligochaetes collected from areas contaminated by copper and zinc in British Columbia.

Petersen and Petersen (1983) reported that net-spinning caddisfly larvae of the genus <u>Hydropsyche</u> (Trichoptera) exhibited anomalies in the structure of their capture nets when collected from stream localities receiving heavy metal and toxic chemical wastes. The frequency of anomalies in a <u>Hydropsyche</u> population increased with proximity to a pollution source.

A number of aquatic vertebrate test species for teratogenesis have been developed, using fish and amphibian species. Of these, the amphibian FETAX system developed at Oak Ridge National Laboratories for testing of complex environmental mixtures (Dumont et

al., 1983) is probably most applicable to sediment testing due to the low-oxygen tolerance of amphibian embryos. Sediment extracts can be applied in the laboratory, or embryos can be reared in situ at the sediment/water interface. Similar teratogenesis test systems have been developed using fish embryos (e.g., Koenig et al., 1982); however, these generally require higher oxygen levels. A major advantage of vertebrate test organisms over invertebrates is that they carry a suite of activating enzymes similar to those of mammals, and thus may be better indicators of potential human health hazards.

As part of their studies on the embryopathic effects of cadmium, mercury and zinc on goldfish, rainbow trout and the narrow-mouthed toad (Gastrophryne carolinensis), Birge et al. (1977) reported that the frequencies of terata appearing in surviving populations ranged from 5 to 31% in egg-through-larvae bioassays performed on metal-enriched sediment, compared to terata frequencies of less than 1% for controls. Frequency of terata produced by sediment metals was highest for mercury and lowest for zinc. Terata frequencies increased proportionately with sediment metal concentration only for the trout exposures.

2.2 Contaminant Release from Sediment

2.2.1 Sediments as a Sink and Source

Sediments are formed from the deposition of particulate organic and inorganic materials that are the products of mechanical, chemical and biological processes. Deposited sediments, therefore, consist of particulate mineral matter, inorganic material of biogenic origin, and organic matter in various stages of decomposition. In natural sediments, these constituents (e.g., sand, silt, clay, precipitates, organic matter) occur in a wide range of proportions depending on geographic and environmental conditions.

Sediments are the principal sinks for heavy metals and organic contaminants in aquatic systems. In the Great Lakes, many contaminants become associated with fine-grained sediment or particulate organic matter (Allan, 1986), and are transported into the depositional basins (e.g., Kemp and Thomas, 1976). The contaminant concentrations in the sediments of individual lake basins reflect the overall loadings to each basin.

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However, contaminant accumulations also can occur in the nearshore zone where shoreline morphometry or man-made structures restrict further transport of fine-grained sediments and associated contaminants into the open lake. Contaminant concentrations in sediments of these sinks reflect loadings from local sources, e.g., tributaries (Fitchko and Hutchinson, 1975). It is at these local sinks, generally in harbours of industrialized centres, that in-place pollutant problems have been identified (IJC, 1983).

Extensive surveys of the contaminants in sediments from harbours have been undertaken and the concentration data have been related to background concentrations or MOE bulk chemical guidelines (Persaud and Wilkins, 1976) for evaluating dredged material for openwater disposal. These surveys include 116 river mouths around the Great Lakes (Fitchko and Hutchinson, 1975) and 78 harbours on the Canadian side of the Great Lakes (Mudroch and Sandilands, 1979; Thomas and Mudroch, 1979). Recently, on the basis of these and other available data, the MOE and the Environmental Protection Service, Ontario Region, have undertaken a complete re-evaluation of the MOE guidelines for open-water disposal of dredged material (Mudroch et al., 1986). This re-evaluation is ongoing.

However, these guidelines, based on total concentrations of contaminants in the sediments, will have little relationship to the potential of sediment-associated contaminants to act as a pollution source to the water column.

Many studies have shown that much of the total concentration of heavy metals in sediment material is not readily solubilized, as it is associated with such less reactive phases, e.g., in the mineral lattice of crystalline solids, strongly sorbed to particulate surfaces, and in organic materials (Gibbs, 1973; Walters and Wolery, 1974; Brannon et al., 1976a). Similarly, organic compounds, such as PCBs and organochlorine pesticides, generally have a low solubility and are tightly sorbed by clay particles (Pionke and Chesters, 1973; Karickhoff et al., 1979).

However, significant remobilization of contaminants, especially heavy metals, from polluted bottom sediments to the water column can occur due to physicochemical changes at the sediment-water interface such as physical disturbance, e.g., dredging, bioturbation, or alteration of dissolved oxygen concentrations. Release of toxic organic contaminants from bottom sediments is also expected (Allan, 1986). Apparently, all hydrophobic compounds may be completely extracted from sediment by water alone, if sufficient time (e.g., 131 days for 1,3,5-TCB at 4°C) is available (Oliver, 1985).

2,2,2 Metal Contaminant-Sediment Interactions

There are several processes of removal of heavy metals from water to sediments. The dominant process, of course, is sedimentation. The suspended particulate matter, with metals sorbed to its surface, is deposited when the hydrodynamic forces are no longer competent to maintain it in the water column. Secondly, sorption of dissolved metals can occur directly by the bed sediments. This primarily involves precipitation and coprecipitation, organic matter complexation, and adsorption by the sediment grains, especially clay (Leland et al., 1973). Finally, uptake of metals from the water by the plankton and other biota will result in eventual additions to the sediments following death. The efficiency of this metal transport to the sediments depends on the rate of decay of the organism (Boothe and Knauer, 1973). Decomposition proceeds during settling and continues at the sediment-water interface, resulting in metal additions during burial.

The concentration of heavy metals in lake sediments can be related to a number of first and second order factors (Hutchinson and Fitchko, 1984). The first order factors involve the amount of metal input to lakes which is dependent on the magnitude and nearness of urban-industrial and agricultural sources, geology, rates of erosion, climate, efficacy of pathway transport, and the geomorphological characteristics of the drainage basin. Second order factors involve the binding and retention mechanisms, such as cation exchange capacity, mineralogical and chemical composition, the amount of organic matter and the percentage of fine sediment. These mechanisms are affected by physical disturbances, such as water currents, dredging, shipping activity, etc., and the geochemical and biological mobilizations of the metals.

A number of studies have been undertaken to determine the relationship between heavy metal concentrations and various sediment parameters. For example, the following correlations were reported by Shimp et al. (1971): chromium with organic carbon and iron oxide content; copper with organic carbon, iron oxide content, amount of clay and manganese oxide content; lead with organic carbon; manganese with iron oxide content; nickel with iron oxide content and clay amount; and zinc with organic carbon. Oliver (1973) reported that concentrations of copper, chromium, lead, manganese, nickel and zinc were correlated with the surface area of the sediment particles, i.e., the metal concentrations increae with decreasing particle size. Thomas (1972) found that the concentration of mercury was correlated with grain size, clay, organic carbon, iron and

sulphur content. Fitchko and Hutchinson (1975) found that copper, lead, manganese, mercury, nickel and zinc concentrations were correlated with organic content and percent clay.

These data, as well as numerous other studies (e.g., Jenne, 1968; Nriagu and Coker, 1980; Lion et al., 1982; Reimers and Krenkel, 1974; Takamatsu et al., 1980) indicate that the primary physicochemical sorption processes for sorption of metals in sediments are adsorption onto the exchange surfaces of the finer sediment particles, precipitation and coprecipitation, particularly with hydrated iron and manganese oxides, and complexation with organic particulate matter. The release of heavy metals from the sediment is influenced by a number of physical, chemical and biological parameters, and can substantially affect the quality of overlying water.

Physical disturbances involve the reworking and/or resuspension of sediments by hydrodynamic forces (water currents, wave action) and anthropogenic activities (ship passage, dredging activities). The displaced sediments may be exposed to a different physicochemical regime which may affect metal sorption and mobilization.

A considerable amount of work has been undertaken at the U.S. Army COE Waterways Experiment Station, Vicksburg, Mississippi, as part of the Dredged Material Research Program, to evaluate the potential for contaminant release to the water column during open-water dredged material disposal. The standard elutriate test was designed to simulate the dredging and disposal process (U.S. EPA/U.S. COE, 1977). In the test, sediment and dredging site water are mixed in the ratio of 1:4 by volume. The mixture is shaken for 30 minutes, allowed to settle for one hour, centrifuged and filtered through a 0.45 u filter. The filtered water (elutriate water) is then analyzed for chemical constituents. Moreover, a sample of the dredging site water used in the elutriate test is filtered through a 0.45 u filter and analyzed for the same chemical constituents. A comparison of elutriate water with the filtered dredging site water for like constituents indicates whether a constituent is or is not released in the test. Dredged materials are not considered to be potentially environmentally deleterious when the concentrations of major constituents in the standard elutriate do not increase 1.5 times above the ambient site water concentrations. The elutriate test may represent conditions of natural water turbulence when bottom sediments are resuspended in the water column and associated contaminants are solubilized into the water column.

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Manganese is the only metal released in substantial quantities during elutriate tests and aquatic disposal (Brannon, 1978). Manganese, however, is generally not toxic, and is an essential micronutrient. The most stringent standards for manganese (0.05 mg/L) are based on aesthetic considerations for potable water. Tolerance values reported for freshwater life range from 1.5 to 1,000 mg/L (U.S. EPA, 1976). The slightly elevated manganese concentrations reported for disposal site waters shortly following disposal were well below the critical tolerance range.

Consistent release of trace metals other than manganese has not been observed during studies of the elutriate test of dredged sediments (Brannon, 1978). Transitory releases (duration of a few minutes) of mercury (0.01 to 0.05 ug/L), lead (less than 0.04 mg/L), cadmium (0.00008 to 0.0025 mg/L) and nickel (0.005 to 0.020 mg/L) have been observed on occasion during dredge spoil disposal. Iron is usually released initially in much higher concentrations than metals other than manganese. However, released iron is subject to very rapid oxidation and precipitation in the water column. As discussed previously, the precipitation of iron oxides will tend to remove other metals from solution by coprecipitation and sorption processes. Large releases of zinc have been observed during elutriate tests under anoxic conditions, but not during aerated elutriate tests. Aerated conditions generally prevail during dredging and disposal operations, as well as during periods of natural resuspension of bottom sediments as a result of water turbulence.

Temporal limnological alterations, such as changes in biological productivity and lake stratification processes, can significantly affect the physicochemical regime at the water-sediment interface. For example, changes in redox potential or pH can result in transformations of metals between geochemical forms affecting their mobilization from the sediment (Gambrell et al., 1976). The most favourable conditions for metal release are reducing conditions (low redox potential) in the sediments and low oxygen concentrations in the overlying waters. With decreasing oxygen concentrations, some contaminants tend to be more soluble, and numerous studies have reported increased concentrations of iron and manganese, as well as other metals, when conditions change from oxic to anoxic at the sediment-water interface (Mortimer, 1941, 1942; Krauskopf, 1957; Gambrell et al., 1976; Aggett and O'Brien, 1985; Sakata, 1985; Brannon and Patrick, 1987). In contrast, the occurrence of high oxygen concentations in the overlying water will result in the precipitation of iron and manganese as hydrous oxides which will scavenge (coprecipitate) other heavy metals from the water column (Jenne, 1968; Murray, 1975; Swallow et al., 1980). Forstner (1982) reported that, in lakes affected by

acid precipitation, significant releases of zinc and nickel were found primarily from the easily reducible sediment fractions. Cadmium was also released mainly from organic phases. In pH-buffered, hard water systems, immobilization by carbonate precipitation seemed to provide an effective mechanism for the reduction of dissolved releases of zinc and cadmium to overlying waters.

Metals can also be mobilized by complexation to dissolved and particulate organic matter. For example, in a study of the partitioning of mercury into sediment phases in the St. Clair River, Cline et al. (1973) reported that direct complexing of mercury to dissolved and particulate organic substances and the formation of an organic-mercury floc may be an important mobilization pathway. Piemontesi and Baccini (1986) postulated that, under reducing conditions at the water-sediment interface, copper in interstitial water is complexed by dissolved organic matter and refluxed to the hypolimnion.

The partitioning or fractionation of heavy metals in sediments among the various geochemical phases has been used by a number of investigators to assess the potential environmental impacts of contaminated sediments, i.e., contaminant release to overlying water and uptake by biota (e.g., Cline et al., 1973; Brannon et al., 1976a; Huang and Liaw, 1978; Menon et al., 1979; Tessier et al., 1984; Jones, 1986).

Analytical procedures involving sequential chemical extractions for the partitioning of trace metals into the various geochemical phases are well established (e.g., Engler et al., 1974; Brannon et al., 1976b; Agemian and Chau, 1977; Malo, 1977; Tessier et al., 1979; Salomons and Forstner, 1980; Van Valin and Morse, 1982; Breward and Peachey, 1983). In general, the sequential extraction procedures result in the chemical fractionation of metals in the sediments into operationally defined categories, e.g., interstitial, easily exchangeable, carbonate-bound, iron/manganese oxide-bound, organically-bound, and residual.

Metals dissolved in interstitial water are considered most available to biota. For example, Prosi (1981) found interstitial water to be the major source of cadmium to <u>Tubifex</u> worms in Rhine River sediments. For example, Prosi (1981) found interstitial water to be the major source of cadmium to <u>Tubifex</u> worms in Rhine River sediments. The easily-exchangeable fraction, characterized by metal ions weakly adsorbed to the

solid phase by cation exchange mechanisms, is also considered readily bioavailable. Exchangeable metals may equilibrate rapidly with the aqueous phase (Gambrell et al., 1976). Metals in the residual fraction are those bound within the structural lattice of the crystalline minerals of the sediment. Metals in this form are unreactive and only slowly become available over geologic time as a result of natural mineral weathering.

In addition to those fractions with readily available and unavailable forms of metals, there are three fractions, i.e., carbonate-bound, iron/manganese oxide-bound and organically-bound, with metal forms that are potentially available. Most of the metals present in sediments fall in this category. Metals in these potentially available forms may possibly be mobilized to more readily bioavailable forms as a consequence of physicochemical changes in the sedimentary environment discussed previously.

A number of biological processes can influence the mobilization of metals from sediments. For example, bioturbation by macroinfauna can increase the penetration of oxygen and the redox potential discontinuity into the sediment, as well as affect pH levels in actively worked substrates (Krantzberg, 1985). These changes have been correlated with metal redistributions among physicochemical forms and the flux of copper, iron, mercury, manganese and zinc to the overlying water (e.g., Granelli, 1979; Krantzberg and Stokes, 1985; Matisoff et al., 1985).

The methylation and mobilization of certain heavy metals in sediments by microorganisms is a biologically significant process (Jernelov, 1975; Beijer and Jernelov, 1979). Bacteria exposed to toxic metals can adapt to detoxify their environment by transforming the metals to other forms. However, these other forms of metals may be more or less toxic to higher organisms.

The methylation of mercury (Jensen and Jemelov, 1969; Wood, 1974) provides a good example. Aerobic bacteria can solubilize mercuric ion from mercuric sulphide by enzymatic oxidation. The solubilized mercuric ion can then be reduced to elemental mercury by other microorganisms. This conversion of mercuric ion to elemental mercury is a detoxification mechanism, since the elemental mercury vaporizes and is lost from the aquatic ecosystem to the atmosphere. Other microorganisms employ a second detoxification mechanism that converts mercuric ion to methylmercury and dimethylmercury. The methylmercury is quickly accumulated by higher organisms,

whereas the dimethylmercury is volatile and is lost to the atmosphere. Finally, other microorganisms can detoxify their environment of methylmercury by reducing it to elemental mercury and methane. For all microorganism to the toxic form of mercury, a relationship occurs between resistance of the microorganism to the toxic form of mercury and its ability to transform this mercury to other less toxic or volatile forms (Summers and Lewis, 1973; Schottel et al., 1974; Nelson and Colwell, 1975).

Methylation as a detoxification mechanism by microorganisms has been shown to occur for other metals, including arsenic (Braman and Foreback, 1973) and lead (Wong et al., 1975).

Processes which influence the aquatic fate of specific heavy metals have been reviewed by Callahan <u>et al.</u> (1979a) and are summarized in Table 2.11.

2.2.3 Organic Contaminant-Sediment Interactions

Organic contaminant-sediment interactions have recently been reviewed by Knezovich et al. (1987). Because of their hydrophobic nature, the organic contaminants addressed in this study initially become associated with suspended particulate materials in the aquatic environment, because the microparticulates provide a large proportion of the total surface area available for adsorption (Lotse et al., 1968; Voice et al., 1983). Most suspended and dissolved materials (i.e., detritus, humic materials, fine-grained clays) have been shown to accumulate hydrophobic organic chemicals that, upon deposition, contribute to the build-up of contaminants in sediment (Carter and Suffet, 1982; Hassett and Anderson, 1982; Means et al., 1982; Nau-Ritter and Wurster, 1983). However, the contaminated sediments can also act as a source of organic contaminants to the overlying waters and atmosphere (Larsson, 1985).

Factors influencing interactions between hydrophobic organic contaminants and sediments include organic carbon content, sediment mineral characteristics (e.g., clay type and content, density, porosity), cation exchange capacity, pH and temperature (e.g., Lotse et al., 1968; Pionke and Chesters, 1973; Choi and Chen, 1976; Karickhoff et al., 1979; Karickhoff, 1980; Carter and Suffet, 1982; Wu and Gschwend, 1986). Pavlou (1980) demonstrated that the adsorption of hydrophobic contaminants on pure inorganic surfaces is negligible, although inorganic particles with natural organic coatings exhibit moderate

					Is the P	Is the Process Important in	
	Aquatic	Aquatic Transport Process ²	ress ²		Determi	Determining Aquatic Fate?2	
			Transport	Photolysis/			Biotransformation/
Contaminant	Volatilization	Sorption	Downstream	Oxidation	Hydrolysis	Bioaccumulation	Biodegradation
Arsenic	YES(I)	YES(I)	YES(1)	NO(3)	YES(I)	YES(2)	YES(I)
Cadmium	NO(2)	YES(I)	YES(1)	NO(3)	YES(I)	YES(I)	NO(3)
Chromism	NO(3)	YES(I)	YES(2)	NO(3)	YES(2)	YES(I)	NO(3)
Copper	NO(3)	YES(1)	YES(I)	NO(2)	YES(I)	YES(I)	NO(3)
Lead	UNCT(1)	YES(I)	YES(1)	(I)NCT(I)	YES(I)	YES(1)	YES(I)
Mercury	YES(I)	YES(I)	YES(1)	YES(2)	YES(I)	YES(1)	YES(1)
Nickel	NO(3)	YES(I)	YES(1)	NO(3)	YES(2)	NO(2)	NO(3)
Selenium	UNCT(2)	YES(I)	YES(I)	NO(3)	YES(2)	UNCT(I)	YES(1)
Zinc	NO(3)	YES(I)	YES(I)	NO(3)	YES(I)	YES(1)	NO(3)

¹ After Callahan et al. (1979a).

² for each chemical and related process, two ratings are presented. The first is a statement of importance and can be one of the following: YES, NO, or UNCT (for uncertain).

The second is a numerical rating, dealing with available supporting data, explained below:

^{(1).} There are environmental data available to support this conclusion.

^{(2).} There are no direct conclusive environmental data; some laboratory data can be extrapolated to support conclusions.

^{(3).} There are no supporting data available; evidence is drawn from theoretical calculations, estimates, results for similar chemicals, and inferences.

to strong binding energies. These observations are consistent with the theory that the sorption of organic contaminants is principally a partitioning process between aqueous and organic phases. Furthermore, Hartung and Klingler (1970) reported that sedimented polluting oils may be an important factor influencing the concentration of hydrophobic contaminants from water, particularly in industrial areas affected by oil pollution.

The partitioning of a hydrophobic organic contaminant between water and sediment is generally predicted by calculating adsorption constants based on the sediment's organic matter content (e.g., Karickhoff, 1980). However, this chemical-organic 'partitioning theory' of sediment adsorption may be too simplistic (Knezowich et al., 1987). The inclusion of the adsorbate and chemical structural parameters may be necessary to increase the predictive accuracy of contaminant sorption models. For example, Jaffe and Ferrara (1984) have recently developed a model, incorporating nine physical and chemical parameters, for predicting sediment-pollutant interactions. The development of such complex models may provide a more precise determination of sediment-sorption interactions and are more likely to have site-specific applications.

Bottom sediments can act as a source of organic contaminants to overlying waters in two ways. Firstly, contaminants may desorb into the interstitial water with subsequent diffusion into overlying water. Secondly, bottom sediments may be resuspended into the water column, where desorption of the contaminants can occur.

Interstitial water plays an important role in sediment-water sorption chemistry and contaminant bioavailability. Interstitial water is formed due to the entrainment of water during the sedimentation process, and is essentially isolated from the water column (Batley and Giles, 1980). The amount of interstitial water available for the desorption of sediment-sorbed organic contaminants depends on sediment porosity, which is determined by particle size distribution and the degree of compaction.

The desorption of sediment-sorbed organic contaminants is mediated by interstitial water, and there is some evidence that the interstitial water concentrations of these contaminants are related to the organic carbon content of the sediment. For example, Adams et al. (in Knezovich et al., 1987) found higher concentrations of Kepone in interstitial water taken from a sediment with low organic carbon content (1.5%) than for that with high organic carbon content (12.0%).

Furthermore, low concentrations of dissolved organic matter and/or non-settling microparticulates or organic macromolecules in the interstitial and overlying water can significantly enhance the solubility and stability of many hydrophobic organic contaminants, notably DDT and some PCB congeners (Gschwend and Wu, 1984; Chiou et al., 1986). The water solubility enhancements can be accounted for by a partition-like interaction of the solute (contaminant) with dissolved organic matter. The extent of solubility enhancement depends on the type of solute and on the concentration and composition of the dissolved organic matter.

Laboratory studies on the desorption of chemicals from sediments have suggested the occurrence of a "residual" or "resistant" component of the organic contaminant content in the sediments. Karickhoff (1980) noted that the longer the incubation time after contaminant spiking, the more difficult it was to desorb the contaminants from the sediments. For 2,4,5,2,4,5-hexachlorobiphenyl, DiToro and Horzempa (1982) and Horzempa and DiToro (1983) found that, while the adsorption process was rapid (minutes to hours), the reverse process was slow, because a significant portion of the sorbed contaminant was highly resistant to release. The adsorption and desorption process was not completely reversible, resulting in a distinction between reversible and resistant desorption components.

These results suggest that, with the cessation of contaminant loadings to an undisturbed sedimentary environment, previously-contaminated sediment would be buried by uncontaminated sediment. Because of the increased resistance of the contaminant with sediment age, together with decreased volume of interstitial water with sediment depth, and slow diffusion rates, the availability of the contaminant to overlying water and benthic biota would be very much reduced.

However, undisturbed sedimentary environments rarely, if ever, occur in freshwater systems. For example, Charleton (1983) and Oliver and Charleton (1984) reported that a sediment layer about 1 mm thick in the sedimentation basins of Lake Ontario is in a constant state of flux. Baker et al. (1985) reported that this benthic nepheloid layer in western Lake Superior was enriched in PCB, p,p-DDE and HCB. Resuspension events resulted in a 50% increase in the PCB burden in the water column. Furthermore, seasonal cycling of PCB congeners was strongly dependent on their degree of chlorination. During stratification, heavier chlorinated congeners were rapidly lost from

the water column under stratification (half-life of 17 to 28 days), presumably due to differential sedimentation and coagulation-flocculation. Conversely, lighter chlorinated PCB congeners apparently migrated from interstitial waters of surficial sediments to the overlying benthic nepheloid layer (2 to 7 mm thick).

In the nearshore environment, surficial sediments are constantly being disturbed and resuspended due to hydrodynamic processes (water currents, wave action), bioturbation and anthropogenic activities (ship movements, dredging activities).

Oliver (1985) undertook laboratory studies of the desorption of chlorinated hydrocarbons from spiked and anthropogenically contaminated sediments. The sediments were suspended in water to simulate natural dynamic conditions. Based on the desorption isotherms, all contaminants associated with the sediment would eventually desorb given sufficient time in clean water. Further calculations based on current loadings to Lake Ontario, for those contaminants with large active sources, the contribution from desorption from bottom sediments was minimal. However, for compounds with decreased ongoing loadings (e.g., HCB), desorption from bottom sediments could play a significant role in controlling lakewater concentrations.

Bioturbation has been shown to be an important process of organic contaminant transport in bottom sediments. For example, Karickhoff and Morris (1985a) reported that over 90% of the hexachlorobenzene present in the sediment reworking zone (6 to 10 cm) of tubificid oligochaetes was transported to the sediment surface during a 30- to 50-day period. Contaminant release into the water column was about five times greater in the presence of worms over a 90-day period.

Processes other than sorption/desorption which influence the aquatic fate of some of the organic contaminants addressed in this study have been reviewed by Callahan et al. (1979a,b) and are summarized in Table 2.12. Volatilization and biodegradation are two important processes affecting the amount of contaminant available for accumulation in the sediment and biota.

Many hydrophobic contaminants have vapour pressures that are sufficiently high so that loss to the atmosphere may be a major fate pathway. Henry's law constants (H) have been used to predict the tendency of a chemical to volatilize from solution, but appear to

					Is the P	Is the Process Important in	
	Aquatic	Aquatic Transport Process ²	7550		Determit	Determining Aquatic Fate ²²	
			Transport	Photolysis/			Biotransformation/
Contaminant	Volatilization	Sorption	Downstream	Oxidation	Hydrolysis	Rioaccumulation	Biodegradation
Aldrin	ITNCT(2)	YES(2)	LINCT(2)	UNCT(2)	(I)ON	YES(1)	YES(2)
ox-RHC	LINCT(2)	UNCT(2)	UNCT(2)	(I)ON	NO(1)	UNCT(I)	YES(2)
A-BHC	(INCT(2)	UNCT(2)	UNCT(2)	(I)ON	(I)ON	UNCT(I)	YES(2)
J-BHC	LINC T(2)	UNCT(2)	UNCT(I)	NO(1)	NO(1)	UNCT(I)	YES(2)
Chlordane	UNCT(2)	UNCT(2)	UNCT(2)	(CLINCT(2)	(I)ON	Y ES(1)	UNCT(2)
DDT	Y ES(2)	YES(1)	UNCT(2)	UNCT(2)	UNCTO	YES(I)	UNCT(2)
Dieldran	LINCT(2)	Y ES(2)	UNCT(2)	UNCT(2)	NO(1)	YES(I)	UNCT(2)
Endrin	FINCT(2)	UNCT(2)	UNC T(2)	LINC T(2)	NO(1)	YES(1)	UNCT(2)
HCR	UNCT(3)	YES(2)	UNCT(3)	NO(3)	NO(3)	Y ES(1)	NO(3)
Heptachlor	UNCT(2)	NO(2)	UNCT(2)	LINCT(2)	YES(1)	UNCT(I)	NO(1)
PCBs	YES(2)	YES(I)	IINCT(3)	UNCT(3)	NO(3)	Y ES(1)	NO(I)

1 After Callahan et al. (1979a, b).

2 for each chemical and related process, two ratings are presented. The first is a statement of importance and can be one of the following: YES, NO, or UNCT (for uncertain). The second is a numerical rating, dealing with available supporting data, explained below:

- (1). There are environmental data available to support this conclusion,
- CD. There are emploitined and available to support this conclusion.
- (3). There are no supporting data available; evidence is drawn from theoretical calculations, estimates, results for smilar chemicals, and inferences. (2). There are no direct conclusive environmental data; some laboratory data can be extrapolated to support conclusions.

predict higher mass transfer coefficients than occur in the environment (Mackay and Yeun, 1980, 1983). This discrepancy may be due in part to the increased retention of environmental contaminants because of their sorption to sediment and suspended particulate matter. For example, Karickhoff and Morris (1985b) reported that desorption was enhanced by air stripping, and consisted of 'fast' and 'slow' phases of contaminant release, with a continuously increasing resistance to desorption. It was concluded that this behaviour may derive from contaminant transport within sediment particles.

Biodegradation is also an important process affecting the amount of contaminant available for accumulation in the sediment and biota. The ability of certain strains of bacteria to degrade organic contaminants in the aquatic environment is a well-established phenomenon (e.g., Pfister et al., 1970; Matsumura et al., 1971; Shiaris and Sayler, 1982). However, the rate of biodegradation and therefore the extent of persistence of the organic contaminant are dependent on a number of factors, including contaminant toxicity, chemical structure, the presence of other organic compounds to serve as a carbon and energy source, and the physicochemical regime.

In summary, chemicals that are hydrophobic and non-volatile are likely to have relatively high sediment concentrations due to their depletion in the water column by sedimentation processes and their relative persistence. Contaminants that persist beyond the relatively rapid initial phase of desorption and volatilization would likely still be available to benthic biota (see Section 2.3) due to the dynamic nature of the sedimentary environment.

2.2.4 Extent of the Database

A considerable amount of data is available on the release of contaminants in sediment to interstitial and overlying waters. Studies relating concentrations of specific contaminants in sediments to contaminant concentrations in interstitial and/or overlying water are listed in Table 2.13. The actual sediment and water contaminant concentration data from many of these studies have been tabulated into a spreadsheet database format. Examples of this database are presented in Appendices 1 and 3.

The isolation of interstitial water is critical to contaminant-sediment sorption/desorption studies and has been accomplished by a variety of methods (Knezovich et al., 1987).

TABLE 2.13: STUDIES RELATING CONCENTRATIONS OF SPECIFIC CONTAMINANTS IN SEDIMENTS TO CONCENTRATIONS IN OVERLYING AND/OR INTERSTITIAL WATER

Contaminant	Reference*
As	Giddings and Eddleman (1977), Brannon and Patrick (1987)
As, Cd, Cu, Cr, Pb, Hg, α -BHC, γ -BHC, p,p-DDD, heptachlor, heptachlor epoxide	Popp <u>et al.</u> (1983)
Cd, Cr, Cu, Ni, Zn	Malueg <u>et</u> <u>al.</u> (1984b)*
Cu, Pb	Brown (1976)
Cd, Cr, Cu, Pb, Ni, Zn	Chapman <u>et al.</u> (1986)
Cu, Zn	McMurtry (1982)
Hg	Turner and Lindberg (1978)*
Cu ¹	Kosalwat and Knight (1987b)*
Cd, Cr, Cu, Fe, Pb, Mn, Ni, Zn	Neff <u>et al.</u> (1978)
Cd, Hg	Salamon (1984)*
Cd, Hg, Zn	Birge <u>et al.</u> (1977)
Cu	Cairns <u>et al.</u> (1984)*, Malueg <u>et al.</u> (1984a)*
As, Cd, Cr, Cu, Fe, Pb, Mn, Hg, Ni, Zn	Prater and Hoke (1980)*
As, Cd, Mn, Ni, Zn	Brannon <u>et al.</u> (1976a)*
Cd	Francis <u>et al.</u> (1984)*, Nebeker <u>et al.</u> (1986a)*
Cd, Cu, Mn, Zn	Menon <u>et al.</u> (1977)*
Cd, Pb, PCB	Tatem (1986)*
As, Cd, Cr, Cu, Fe, Pb, Mn, Hg, Ni, Zn, aldrin, β -BHC, γ -BHC, γ -chlordane, o,p-DDT, p,p-DDD, p,p-DDT, p,p-DDE, dieldrin, endrin, HCB, mirex, PCB	Prater and Anderson (1977b)*

TABLE 2.13: STUDIES RELATING CONCENTRATIONS OF SPECIFIC CONTAMINANTS IN SEDIMENTS TO CONCENTRATIONS IN OVERLYING AND/OR INTERSTITIAL WATER

Contaminant	Reference*
As, Cd, Cr, Cu, Fe, Pb, Mn, Hg, Ni, Zn	Prater and Anderson (1977a)*
As, Cd, Cr, Cu, Fe, Pb, Mn, Hg, Ni, Zn, PCB	Bahnick <u>et al.</u> (1981a)*
PCB (HCBP)	Muir <u>et al.</u> (1983)
PCB	Eadie <u>et al.</u> (1982c)*
Pb	Newman and McIntosh (1982)
Cd, Cr, Cu, Fe, Pb, Mn, Hg, Zn	Weber and Posner (1974)*
Hg	Cline et al. (1973), Walters and Wolery (1974)
Zn	Koivo and Oravainen (1982)
Cd, Cr	Gilbert <u>et al.</u> (1976)

¹ Substrate consists of Cerophyl.

^{*} Sediment and overlying/interstitial water contaminant concentration data in computer database (see Appendices 1 and 3).

Some of these methods, e.g., centrifugation, however, may not be suitable for the analysis of hydrophobic organic contaminants which may be affected by rapid partitioning processes.

A cursory review of available data from the studies listed in Table 2.13 indicated that the concentrations of metals in interstitial water were generally higher than metal levels in overlying water. For example, Bahnick et al. (1981a) reported that, compared to the overlying water, the unfiltered interstitial water was generally greatly enriched in iron (by factors of 15 to 100), manganese (by factors of 10 to over 100) and mercury (by factors of 5 to 20), even though the concentrations of suspended solids were very similar (Table 2.14). In addition, the interstitial water generally contained higher amounts of arsenic and about two to ten times as much chromium and zinc. Even in the filtered interstitial water samples, iron and manganese concentrations were generally two to 100 times greater than in the overlying water.

Popp et al. (1983) reported that, for aerobic surficial sediments collected from river locations, metal (As, Cd, Cu, Cr, Pb) concentrations in interstitial water were similar to those in overlying water. However, for reservoir surficial sediments, the concentrations of cadmium, copper, chromium and lead were consistently higher in the interstitial sediments than in bottom water. In the case of cadmium, concentrations were about an order of magnitude higher in interstitial water.

A number of laboratory studies involving sediments enriched with metals have indicated a strong correlation between metal concentrations in the sediments and metal levels in the overlying water (Birge et al., 1977; Francis et al., 1984). This can be expected since the physicochemical characteristics affecting metal sorption/desorption are relatively constant in the homogenized sediment subsamples. This relationship between metal concentrations in sediment and overlying water can be expected to be less evident in natural aquatic systems due to the marked heterogeneity of the sedimentary environment. Based on analysis of the MOE In-Place Pollutants Program database, good correlations between bottom water and interstitial water were obtained for arsenic, copper, manganese and nickel (Section 3.1.1).

In the case of organic contaminants, concentrations measured in interstitial and overlying water were generally below the detection limit. As a result, it is difficult to

Table 2.14: $\begin{array}{c} \text{Comparison of metal concentrations in overlying and} \\ \text{Interstitial waters}^I \end{array}$

	Concentration (ug/L)			
	Overlyi	ng Water	Interstiti	al Water
Contaminant	Mean	Range	Mean	Range
Arsenic	3.0±1.4	(1.7-6.0)	4.6±1.2	(2.8-6.1)
Cadmium	0.13±0.22	(<0.05-0.67)	0.61±0.87	(<0.05-2.0)
Chromium	0.7±0.8	(<0,2-2,5)	3.2±2.8	(0.5-7.1)
Copper	35±33	(2.1-97)	40±49	(11-153)
Iron	398±162	(230-670)	7,809±7,008	(570-21,400)
Lead	2.5±2.5	(1.0-8.1)	7.9 _± 7.7	(0.9-23)
Manganese	62±54	(24-170)	2,856±2,119	(540-6,000)
Mercury	0.06±0.01	(<0.05-0.08)	0.64±0.55	(0.05-1.7)
Nickel	2.3±0.6	(<2-3,6)	3.7±3.1	(<2-9.5)
Zinc	6.3±5.8	(2,5-20)	22±23	(7-68)

¹ After Bahnick <u>et al.</u> (1981a).

make, based on these data, any generalizations regarding the role that interstitial water plays in the bioavailability of organic contaminants. The prediction of the potential for organic contaminant release must, therefore, likely be based on data on water solubility, octanol-water partition coefficient and bioconcentration factor.

However, Adams et al. (in Knezovich et al., 1987) reported that Kepone concentrations in interstitial waters were higher than those in the overlying water under flow-through conditions in the laboratory. These data suggest that the interstitial water is important as a medium influencing the uptake of organic contaminants by benthic biota.

2.3 Review of Bioaccumulation and Biomagnification Data

2.3.1 Extent of the Database

Bioaccumulation, biomagnification and bioconcentration have been defined by Persaud and Lomas (1987) as follows:

- Bioaccumulation uptake and retention of environmental substances by aquatic organisms from both the environment (water, sediment) and food.
- Biomagnification the magnification (increase in concentration) of an environmental substance through the food chain.
- Bioconcentration uptake and retention of environmental substances by the organism from ambient air, water or sediment.

The database compiled on bioaccumulation of the contaminants by benthic macroinvertebrates and bottom-dwelling fish is quite extensive. Studies relating benthic macroinvertebrate and bottom-dwelling fish bioconcentration to contaminant levels in sediments are listed in Tables 2.15 and 2.16, respectively. Contaminant concentration data from most of these studies have been tabulated into a spreadsheet database format. An example of this database is presented in Appendix 3.

Bioconcentration factors (BCFs) for each contaminant tend to be variable. Some of this variation may be due to differences in the weight basis (wet vs. dry) for expressing tissue and sediment concentrations, and differences in tissues considered (whole organism, gut-corrected, lipid-normalized); however, most of the variation can probably be attributed

TABLE 2.15: STUDIES RELATING BENTHIC MACROINVERTEBRATE BIOCONCENTRATION TO CONTAMINANT LEVELS IN SEDIMENT

Contaminant	Reference*
As	Giddings and Eddlemon (1977), Wagemann et al. (1978)*
As, Cd, Cr, Cu, Fe, Hg, Mn, Zn	Cherry <u>et al.</u> (1979)
As, Cd, Cr, Cu, Mn, Hg, Zn	Cherry and Guthrie (1977)*
As, Cd, Cr, Cu, Pb, Hg, Ni, Zn	Heit <u>et al.</u> (1980)*
As, Cd, Cr, Cu, Fe, Pb, Mn, Hg, Ni, Zn, PCB	Bahnick <u>et al.</u> (1981a)
As, Cd, Pb, Mn, Hg	Hartung (1974)*
As, Cd, Cu, Fe, Pb, Mn, Hg, Ni, PCB, aldrin, α-BHC, β-BHC, γ-BHC, DDT, dieldrin	Acres (1983)*
Cd, Cr, Cu, Fe, Pb, Mn, Hg, Ni, Zn	Neff <u>et al.</u> (1978), Fitchko (1987b)
Cd, Cr, Cu, Fe, Mn, Hg, Zn	Guthrie and Cherry (1979)*, Copeland and Ayres (1972)*
Cd, Cr, Cu, Pb, Ni, Zn	Mathis and Cummings (1971, 1973)*
Cd, Cu, Fe, Pb, Mn, Hg, Ni, Zn	Chapman et al. (1980)*
Cd, Cu, Fe, Pb, Mn, Zn	Wickham <u>et al.</u> (1987)*
Cd, Cu, Pb, Zn	Anderson and Brower (1978)*
Cd, Pb	Enk and Mathis (1977)*, Czarnezki (1987)*
Cd, Pb, Ni, Zn	Van Hassel <u>et al.</u> (1980)*
Cd, Mn, Pb	Mathis <u>et al.</u> (1977)
Cd, Cr, Cu, Fe, Pb, Mn, Ni, Zn, PCB	McKee <u>et al.</u> (1985)*
Cu	Kosalwat and Knight (1987b)*
Cu, Fe, Zn	Brown (1977)
Cu, Fe, Mn, Zn	Lewis (1980)

TABLE 2.15: STUDIES RELATING BENTHIC MACROINVERTEBRATE
BIOCONCENTRATION TO CONTAMINANT LEVELS IN SEDIMENT

Contaminant	Reference*
Cu, Pb	Brown (1976)*
Cu, Mn, Zn	Seagle and Ehlmann (1975)*
Cu, Pb, Zn, Fe, Mn	Tessier <u>et al.</u> (1984)*
Cu, Hg	Salamon (1984)*
Cu, Ni, Zn	Hutchinson <u>et al.</u> (1975)*, Walters <u>et al.</u> (1972), Moriarity and French (1977)
Cr, Fe, Mn, Zn	Shuman <u>et al.</u> (1977)*
Pb	Newman and McIntosh (1982*, 1983*), Leland and McNurney (1974)*, Pace and DiGiulio (1987)
As, Cd, Cu, Mn, Pb, Hg, Zn, DDE, DDD, DDT, dieldrin, PCB	Greichus <u>et al.</u> (1977*, 1978*)
Pb, Hg	Bissonnette (1977)
Pb, Mn, Zn	Drifmeyer and Odum (1975)
Нg	Skoch and Sikes (1973)*, Hildebrand et al. (1976, 1980), Jernelov and Lann (1971)*, Rada et al. (1986)*, Moriarity and French (1977), Potter et al. (1975)*, Norstrom and Peter (1972)*, Copeland (1972)*, Hamilton (1972a, b*), Surma-Aho et al. (1986)*, Wren and MacCrimmon (1986)*, Richins and Risser (1975)
Hg, Zn	Magnuson <u>et al.</u> (1976)*
Hg, Zn, DDT, mirex, PCB	Niagara River Toxics Committee (1984)*
Hg, PCB	Mac and Willford (1986)
Zn, PCB	Mac <u>et al.</u> (1984)*
PCB	Meier and Radiske (1984), Lynch and Johnson (1982), Pugsley <u>et al.</u> (1985)*, Veith <u>et al.</u> (1977)*, Swindoll (1986), Muir <u>et al.</u> (1983)*

TABLE 2,15: STUDIES RELATING BENTHIC MACROINVERTEBRATE BIOCONCENTRATION TO CONTAMINANT LEVELS IN SEDIMENT

Contaminant	Reference*
PCB, γ-BHC, chlordane, DDD, DDE, HCB	Smith <u>et al.</u> (1985)*
PCB, HCB	Fox et al. (1983)*
DDT, DDE, DDD	Hickey <u>et al.</u> (1966)*
o,p-DDT, p,p-DDT, p,p-DDD, p,p-DDE	Reich et al. (1986)*
Dieldrin	Rosenberg (1975)*
DDT	Bridges <u>et al.</u> (1963)*
DDT, DDE, DDD, dieldrin, PCB	Haile <u>et al.</u> (1975)*
BHC, endrin, DDT, DDE, DDD, dieldrin, mirex, PCB	Niethammer <u>et al.</u> (1984)*
γ -BHC, aldrin, dieldrin, total DDT	Hannon <u>et al.</u> (1970)*
DDD, DDE, DDT, dieldrin, endrin	Moubry et al. (1968)*, DouAbul et al. (1987)
As, Cd, Cr, Cu, Fe, Pb, Mn, Hg, Ni, Zn, DDT, PCB	Tatem (1986)*
p,p-DDE, HCB, mirex, PCB	Oliver (1984)
As, Cu, Fe, Pb, Hg, DDT, mirex, PCB	MOE (1981)*

^{*} Sediment and benthic macroinvertebrate contaminant concentration data in computer database (see Appendix 3).

TABLE 2.16: STUDIES RELATING BOTTOM-DWELLING FISH
BIOCONCENTRATION TO CONTAMINANT LEVELS IN SEDIMENTS

Contaminant	Reference*
As	Wagemann <u>et al.</u> (1978)
As, Cd, Cr, Cu, Pb, Mn, Hg, Ni, Zn	Hesse and Evans (1972)
As, Cd, Pb, Hg, Zn	Winger and Andreasen (1985)*
As, Cd, Pb, Mn, Hg	Hartung (1974)*
As, Cr, Fe, Hg, Ni, Zn, PCB, DDT	Seelye <u>et al.</u> (1982)
Cd	Francis et al. (1984)*
Cd, Cu	Prahalad and Seenayya (1986)*
Cr, Fe, Mn, Zn	Shuman <u>et al.</u> (1977)*
Cd, Cr, Cu, Fe, Pb, Mn, Hg, Ni, Zn	Fitchko (1987b)
Cd, Cr, Cu, Fe, Mn, Hg, Zn	Guthrie and Cherry (1979)
Cd, Cr, Cu, Pb, Ni, Zn	Mathis and Cummings (1971, 1973)*
Cd, Cu, Pb, Zn	Delisle <u>et al.</u> (1975)*
Cd, Mn, Pb	Mathis <u>et al.</u> (1977)
Cd, Pb	Moriarity et al. (1984)*, Enk and Mathis (1977)*
Cd, Pb, Ni, Zn	Van Hassel <u>et al.</u> (1980)*
Cu, Fe, Mn, Zn	Lewis (1980)
Pb	Chau <u>et al.</u> (1985), Leland and McNurney (1974)
Pb, Mn, Zn	Drifmeyer and Odum (1975)
Hg	Jernelov and Lann (1971), Richins and Risser (1975), Birge et al. (1977), Gregory (1978)*, Hildebrand et al. (1976, 1980), Rada et al. (1986), Konrad (1972)*, Gillespie (1972), Wren and MacCrimmon (1986)*, Weis et al. (1986)
Hg, PCB	Mac and Willford (1986)

TABLE 2.16: STUDIES RELATING BOTTOM-DWELLING FISH
BIOCONCENTRATION TO CONTAMINANT LEVELS IN SEDIMENTS

Contaminant	Reference*
Zn, PCB	Mac et al. (1984)*
DDT	Bridges <u>et al.</u> (1963)*
PCB	Veith <u>et al.</u> (1977)*, Sullivan <u>et al.</u> (1983), Swindoll (1986)
PCB, α -BHC, β -BHC, chlordane, DDT, DDE, DDD, HCB	Smith <u>et al.</u> (1985)*
PCB, DDT, Dieldrin	Lueschow (1972), Haile <u>et al.</u> (1975)*, Perry (1979)
Dieldrin	Morris <u>et al.</u> (1972)*
Mirex	Skaar <u>et al.</u> (1981)
p,p-DDE, p,p-DDD, p,p-DDT, dieldrin	Frank <u>et al.</u> (1974)*
BHC, endrin, DDT, DDE, DDD, dieldrin, mirex, PCB	Niethammer <u>et al.</u> (1984)*
γ -BHC, aldrin, dieldrin, total DDT	Hannon <u>et al.</u> (1970)*
DDD, DDE, DDT, dieldrin	Bevenue <u>et al.</u> (1972)
DDD, DDE, DDT, dieldrin, endrin	Moubry <u>et al.</u> (1968)*, DouAbul <u>et al.</u> (1987)
As, Cd, Cu, Cr, Pb, Hg	Popp <u>et al.</u> (1983)
НСВ	McFarland and Peddicord (1986)
Cd, Cu, Fe, Pb, Mn, Hg, Ni, Zn, aldrin, a-BHC, Y-BHC, a-chlordane Y-chlordane, o,p-DDT, p,p-DDD, p,p-DDE, p,p-DDT, dieldrin, endrin, HCB, heptachlor, heptachlor epoxide, mirex, PCB	McCrea <u>et al.</u> (1984)
γ-BHC	Mostafa <u>et al.</u> (1987)

 $[\]mbox{*}$ Sediment and bottom-dwelling fish contaminant concentration data in computer database (see Appendix 3).

to the many biotic and abiotic factors affecting bioaccumulation from sediments (see Section 2.3.2).

Most of the heavy metal contaminants have BCFs that tend to vary around a value of 1.0 - that is, whole sediment and tissue concentrations are approximately equal (Table 2.17). Among the metals, zinc, mercury and cadmium show higher BCFs most frequently. As noted in Section 2.3.2.2, methyl mercury is accumulated more readily than inorganic mercury and may biomagnify in the food chair; thus, higher BCFs for this element are plausible. Among the other metals, lead, arsenic, chromium and iron rarely show BCFs greater than 1.0, indicating that these metals are rarely bioconcentrated relative to sediment. Low bioaccumulation may be attributed to various factors, such as low bioavailabilities of the sediment-associated contaminants, microhabitat factors that isolate biota from the most bioavailable forms, and rapid and efficient clearance of accumulated contaminants by the organisms.

The database on bioaccumulation of organic contaminants from sediments by benthic biota is smaller than the corresponding database on metals. PCBs are an exception to this situation - a considerable number of publications provides information on PCB accumulation by bottom fauna (Tables 2.15 and 2.16). Among the organics, PCBs show the greatest variability in terms of bioconcentration factors, possibly reflecting the relatively large number of studies reporting on PCB accumulation from sediments. For the most part, BCFs for PCBs range between 0.1 and 100, although Muir et al. (1983) reported very high sediment-based BCFs for an isomer of hexachlorobiphenyl (up to 15,000) in laboratory-exposed Chironomus tentans. In contrast, the more recent work of Swindoll (1986) demonstrated a range of BCFs of only 0.45 to 21.43 for C. tentans exposed to hexachlorobiphenyl in sediment. BCFs in this latter study are in agreement with those reported for other PCBs. Some data are also available on DDT and its derivatives for several benthic invertebrates, primarily from Reich et al. (1986). BCFs for DDT and derivatives range over more than five orders of magnitude (0,001 to 500), but typically fall in the range of 1 to 20, indicating relatively little bioconcentration from sediment sources.

Data on uptake of HCB from sediment are available primarily from the work of Fox et al. (1983) on western Lake Ontario and the Niagara River. In this study, HCB was accumulated to greater levels by carp (BCF of 32) than by benthos (BCF of 0.2 to 22),

TABLE 2.17: TYPICAL WHOLE SEDIMENT-BASED BIOCONCENTRATION FACTORS FOR SEDIMENTARY CONTAMINANTS¹

Contaminant	Benthos	Fish
As	1	1
Cd	10	0.01
Cr	0.1	0.1
Cu	1	0.01
Fe	0.1	0.03*
Pb	1	0.1
Mn	1	5*
Hg	0.1-10	0.1-10
Ni	1	I
Zn	1	5
PCBs	0.1-100	25
Aldrin	0.1*	50 ² *
BHCs	5*	10
Chlordanes	2*	<1,000*
DDT	1-20	5
DDD	0.1-10	-
DDE	0.1-100	3
Dieldrin	1-1,000	0.1-10
Endrin	5	8,000*
Hexachlorobenzene	1-10	30*
Heptachlor	400*	30*
Heptachlor epoxide	-	_
Mirex	_	-

Based on a qualitative evaluation of data in Appendix 3. Typical ranges are given for contaminants with reported BCFs spanning four or more orders of magnitude.

² Value reported as aldrin plus dieldrin

^{*} BCFs based only on one or two data points.

suggesting some degree of food chain biomagnification. No studies were found on bioaccumulation of heptachlor or heptachlor epoxide from sediments, and relatively little information was found relating tissue and sediment concentrations for the other organic contaminants addressed in this study. The available data do suggest that these other contaminants are often bioconcentrated.

2.3.2 Factors Affecting Uptake

The mode and kinetics of contaminant uptake from sediments by bottom-dwelling organisms vary considerably among species and even within species, depending on factors such as feeding ecology of the organism, developmental stage, season and history of exposure. In addition, different uptake routes, such as direct uptake from soluble phases and uptake in food, may be expected to contribute variably to contaminant body burdens.

Aquatic organisms can accumulate environmental contaminants via diet and water uptake. Experiments with organochlorine pesticides have provided conflicting information on the relative significance of these two pathways to bioaccumulation in fish (Chadwick and Brocksen, 1969; Macek and Korn, 1970; Eberhardt et al., 1971; Reinhart, 1972; Jarvinen and Tyo, 1978; Ellgehausen et al., 1980), while others have reported similar accumulation patterns for both the food and water pathways for organochlorine pesticides in fish (Shubat and Curtis, 1986). Furthermore, accumulation of organic contaminants and metals from dissolved phases can be passive due to adsorption onto the surface of bottom-dwelling organisms (Derr and Zabik, 1974; Wolmarans and van Aardt, 1985) or active (Zylstra, 1972; Cheng and Sullivan, 1974). Swindoll (1986) reported on the rate of passive uptake of hexachlorobiphenyl by dead midges that was about half the rate of uptake by live midges.

2.3.2.1 Biotic Factors

The degree of contaminant uptake that may occur varies among and within species. Available data on sediment-based bioconcentration factors for various organisms show a wide variation among species for a specific contaminant, even within individual studies (Appendix 3). Brown (1977) reported significantly higher concentrations of copper and zinc in tissues of free-living Trichoptera in comparison with case-dwelling species, and concluded that the differences were attributed to the protection provided by the cases,

and possibly to other ecological differences between the two groups. Similarly, Fox et al. (1983) reported considerable differences between oligochaetes and amphipods from western Lake Ontario in terms of tissue concentrations of PCBs and HCB, with higher concentrations generally found in amphipods. Contaminant uptake by an individual bottom-dwelling species may vary with an array of biotic and abiotic factors, such as season (Landrum et al., 1983), developmental stage (e.g., larvae vs. adult; Rossaro et al., 1986), body size (Kanazawa, 1978), and differences in feeding habits (Collins et al., 1973). The degree of contaminant uptake by bottom-dwelling organisms depends on the balance between uptake and depuration or metabolism, feeding ecology, and microhabitat differences in exposure to sediments and porewater.

Furthermore, the biological community itself strongly influences the physical-chemical environment in the sediment and thus influences bioavailability of contaminants by various processes (Salomons and Forstner, 1984):

- primary productivity influences pH conditions which in turn influences metal chemistry;
- sulphate reduction to sulphide by bacteria facilitates metal sulphide formation;
- o biological activity influences redox conditions and metal redox conversions:
- production of organic matter which may complex with contaminants;
- bioturbation influences sediment-water exchange processes and redox conditions; and
- methylation of some metals (e.g., Hg).

2.3.2.2 Sediment-Contaminant Associations

Although it has generally been observed that the degree of bioaccumulation is related to the degree of sediment contamination by inorganic substances (e.g., Hart et al., 1986b), the availability of trace metals to benthic feeders is intimately dependent upon the physical-chemical forms in which the metals represent in the sediments (Luoma and Bryan, 1976; Bryan and Hummerstone, 1977; Bryan and Uysal, 1978; Luoma and Bryan, 1978; Luoma, 1983; Tessier et al., 1984). Indeed, some bioaccumulation studies have found no correlation between metal levels in benthic organisms and whole sediment (e.g.,

Kristensen, 1982). Most studies have attempted to relate the heavy metal contents of benthic-feeding organisms to a particular chemical fraction or fractions in the surficial sediments, often based on selective or sequential extractions of sediment-bound metals (e.g., Luoma and Bryan, 1978, 1979; Diks and Allen, 1983; Tessier et al., 1984). The sequential extraction procedure developed by Tessier et al. (1979) partitions sediment-associated metals into five fractions: exchangeable metals, carbonate bound, Fe-Mn bound metals, metals bound to organic matter and sulphides, and residual metals. Bioaccumulation studies applying sequential extraction techniques have typically shown that tissue concentrations in benthic invertebrates correlate best with one or more of the easily extractable fractions, rather than to total sediment metals (Tessier and Campbell, 1987).

Andrews et al. (1985) developed a procedure using radiolabelled metals in combination with sequential extraction in bioaccumulation studies in order to provide greater information on the specific fractions of sediment metals that are bioaccumulated. Briefly, this technique uses radiotracers to label chemical fractions of heavy metals in sediments. The specific activity of the label on worms grown on these sediments should, in theory, approach the specific activity of the label in the biologically available fraction(s) of the sediments. Use of radiolabelled metals in sediment bioaccumulation studies avoids the problem of attempting to correlate total body burdens and concentrations in different sediment fractions. Andrews et al. (1985) used this approach to determine that the easily-exchangeable cobalt fraction was the most probable source of this metal to <u>Tubifex</u> worms fed on natural Ottawa River sediments labelled with cobalt-60. Further studies, using zinc-65 in Toronto Harbour sediments, suggested that the Fe/Mn oxide-bound fraction served as the likely source of zinc to <u>Tubifex</u> (BEAK, 1987b).

Some metals, notably mercury, arsenic, lead and tin, may occur to varying degrees in alkylated forms in the aquatic environment. Most aquatic methylation processes occur in sediments due to bacterial action; thus, benthic feeders are important in the initial transfer of organometals into the food web (Allan, 1986). Generally, methyl forms of metals are more lipophilic and bioavailable than are the inorganic forms. Numerous studies have established that methylmercury is several times more bioavailable and toxic to biota than are inorganic forms (Luoma, 1983). Organic arsenic, however, does not appear to be highly toxic and is readily excreted by most species (Luoma, 1983).

The oxidation state of metals may also influence their bioavailabilities (Luoma, 1983). For example, Hg^0 is more available than Hg^{2+} because of the greater lipid solubility of the former. Likewise, Cr^{6+} is more bioavailable in general than Cr^{3+} . The oxidation state of di- and polyvalent metals will in turn be sensitive to reduction-oxidation conditions in the sedimentary environment.

Among organic contaminants, the most frequently identified contaminant property affecting uptake by aquatic biota is the octanol-water partition coefficient, as well as other measures of hydrophobicity. Various models have been developed that relate octanol-water partitioning to the water-based bioconcentration factor and rates of uptake and clearance by fish (e.g., Neely et al., 1974; Chiou et al., 1977; Veith et al., 1979; Hawker and Connell, 1985) and benthos (Lohner and Collins, 1987). Investigations of factors influencing uptake of organic compounds by bottom-dwelling organisms are relatively few, apart from the general observation that high levels of tissue contamination and sediment contamination generally coincide (e.g., Pugsley et al., 1985; Hart et al., 1986b), and that the degree of sediment contamination is related to the octanol-water partition coefficient and sediment organic content (Karickhoff et al., 1979). Connor (1984, 1985) and Breck (1985) proposed a model relating sediment contaminant levels to levels in fish tissue, based on sediment organic content and octanol-water partitioning, and demonstrated the model using PCB data. McFarland (1984) and Rubinstein and Lake (1986) proposed a bioaccumulation model for uptake from sediments by benthos, based on the lipid content of the organisms, sediment organic content and whole sediment concentration. This latter model has not been previously tested for general application in predicting bioaccumulation from sediments, but is tested using the MOE In-place Pollutants Program database in Section 3.0 of this report.

Sediment particle size may also influence the bioavailability of sediment-associated contaminants. In particular, deposit feeding benthic organisms are limited in terms of the particle size that may be ingested. For instance, Eadie et al. (1982b) found that concentrations of polycyclic aromatic hydrocarbons in Lake Michigan amphipods were more closely correlated with contaminant concentrations in the fine fraction rather than in whole sediment. In a bioaccumulation experiment with PCB-contaminated sediments, Lynch and Johnson (1982) found that bioavailability to amphipods was influenced by particle size, although organic content was a more important factor. Increases in sediment surface area (i.e., decreases in particle size) can also reduce the bioavailability

of contaminants by providing greater numbers of binding sites in the sediments (Swindoll, 1986).

2.3.2.3 Other Factors Modifying Uptake

The bioaccumulation of sediment-associated metals can be influenced by several other environmental factors, in addition to those discussed previously. Among these, temperature (Luoma, 1983; Graney et al., 1984), physical sediment disturbance (Delisle et al., 1975), pH (Graney et al., 1984; Lewis and McIntosh, 1986; Weis et al., 1986) and redox (Luoma, 1983; Allan, 1986) are important. Temperature influences the rate of chemical and biochemical reactions, thus influencing metal bioavailability. Physical disturbance of the sediments by current action can lead to sediment resuspension which in turn influences particle-water interactions. The pH level plays a role in affecting adsorption/desorption reactions through competition between metal cations and protons for binding sites on particles. As discussed previously, redox conditions control oxidation-reduction.

Other water quality conditions may also influence the bioaccumulation of metals by bottom-dwelling animals. Dissolved organic matter may complex with metals released into sediment pore water or into the overlying water column, thereby reducing bioavailability, as demonstrated with <u>Daphnia</u> and <u>Chironomus</u> in copper bioaccumulation studies (Dodge and Theis, 1979; Winner, 1985). Water hardness may influence bioaccumulation of metals released from sediments, as demonstrated in studies of bioaccumulation from water. Calcium and magnesium ions are thought to compete with other metal cations for organic uptake sites, thereby reducing metal uptake in hard waters, as reported for zinc (Luoma, 1983), copper (Winner, 1985) and cadmium (Wright, 1980), although the role of hardness in bioaccumulation of metals from sediment has apparently not been reported. Metals in mixtures may also compete for binding sites on organic molecules, resulting in antagonistic effects, as shown in bioaccumulation studies using Cd-Zn and AR-Cu combinations (Luoma, 1983).

Uptake of organic toxicants by bottom-dwelling organisms is also affected by an array of other physical and chemical factors in the environment. Again, temperature may be expected to influence the rate and degree of accumulation through its effect on respiration rates and aqueous solubilities, as measured for PAH uptake from sediment

and depuration in Great Lakes amphipods (Landrum et al., 1983). Swindoll (1986) reported that the rate of hexachlorobiphenyl uptake by C. tentans from sediment varied directly with temperature, although the steady-state BCF was not significantly affected by temperature. While the role of physical disturbance of sediments on organic contaminant uptake has apparently not been studied, organic contaminants have been identified in nepheloid layers of suspended sediments in the Great Lakes (Eadie et al., 1982c: Baker et al., 1985), and contaminant translocation can be assumed to influence organism exposure. Opperhuizen and Schrap (1987) found that uptake of PCBs from water by guppies was independent of dissolved oxygen concentration over a range of 2.5 to 8 mg/L, and concluded that diffusion rate rather than ventilation volume limited the rates of uptake and depuration from water in fish. Many studies have shown that organic complexing agents (dissolved organic carbon) reduce the bioavailability of hydrophobic organics to aquatic biota (Landrum et al., 1985, 1987; McCarthy and Jimenez, 1985; McCarthy et al., 1985; Carlberg et al., 1986; Kukkonen and Oikari, 1987), although DOC does facilitate transport in the aqueous phase (Landrum et al., 1987). Suspended solids may similarly reduce contaminant availability, as demonstrated for chlordane (Hall et al., 1986). Bioaccumulation and elimination of organic compounds may also show antagonistic interactions when contaminants are present in mixtures (Landrum, 1982; Meier and Rediske, 1984).

2.3.2.4 Water-based Bioaccumulation

While a detailed review and discussion of contaminant bioaccumulation from the aqueous phase is beyond the scope of this report, a brief synopsis of this topic is appropriate here. Contaminant bioaccumulation by aquatic biota has been more frequently related to waterborne contamination rather than to the occurrence of contaminants in aquatic sediments, and water-based bioaccumulation factors have been applied relatively broadly by environmental regulators, managers and scientists in contaminant studies. Because it is the more soluble forms of contaminants in sediments that represent the bioavailable fractions, water-based bioconcentration factors may be useful in evaluating the bioaccumulation potential of contaminants in sediment porewaters to benthic biota.

Table 2.18 provides a summary of water-based BCFs, expressed as: (mass of contaminant/g of tissue)/(mass of contaminant/mL of water). The BCF data in this table are reported for freshwater fish in general and not specifically for bottom-dwelling

TABLE 2.18: WATER-BASED BIOCONCENTRATION FACTORS FOR FRESHWATER BENTHIC MACROINVERTEBRATES AND FISH 1

Contaminant	Ben thos	Fish	
As	333	333	
Cd	4,000	3,000	
Cr	2,000	200	
Cu	1,000	200	
Fe	10-10 ³ *	10 ² -10 ³ *	
Pb	200	60	
Mn	103*	500*	
Hg	100,000	1,670	
Ni	100	40	
Zn	40,000	1,000	
PCBs	10 ⁴ -10 ⁶	10 ⁴ -10 ⁶	
Aldrin	10 ³ -10 ⁴	10 ³ -10 ⁴	
BHCs (based on γ-BHC)	10 ² -10 ³	10 ² -10 ³	
Chlordanes	10 ² -10 ⁴	10 ² -10 ⁴	
TDD	10 ³ -10 ⁵	10 ⁴ -10 ⁵	
DDD	10 ³ -10 ⁴	10 ³ -10 ⁴	
DDE	104	104	
Dieldrin	10 ⁴ -10 ⁵	10 ³ -10 ⁴	
Endrin	10 ⁴ -10 ⁵	10 ³	
Hexachlorobenzene	140-2,700	1,000-15,000	
Heptachlor	104-105	10 ³ -10 ⁴	
Heptachlor epoxide	10 ⁴ -10 ⁵	10 ³ -10 ⁴	
Mirex	-	10 ⁴ *	

¹ Data from Callahan et al. (1979a,b), unless indicated otherwise.

* Other data sources: Fe and Mn (benthos) - Coughtrey and Thorne (1983) Fe and Mn (fish) - CSA (1986)

Mirex - Buckler et al. (1981)

fish. It should also be noted that water-based BCFs do not necessarily denote uptake solely from the water column, but are empirical measures of tissue and water concentrations often taken without regard for the mode of uptake. Water-based BCFs tend to indicate that benthic invertebrates generally accumulate contaminants to higher concentrations than do fish. This may be attributed to the greater degree of contaminant exposure experienced by benthic invertebrates at the sediment-water interface than experienced by fish. Other contributing factors may be their different modes of uptake and surface area to volume ratios. As observed in the sediment-based BCF data (Appendix 3 and Table 2.14), water-based BCFs show that the persistent organic contaminants tend to be accumulated to greater degrees than are the metals.

2,3,3 Biomagnification

Food chain biomagnification occurs if the concentration of a contaminant increases with successive increases in the trophic level. However, well-defined trophic levels often do not exist in aquatic ecosystems, and an individual species may occupy various trophic levels during its lifetime, due to different feeding habits at different life cycle changes. In a review of contaminant biomagnification potential, Kay (1984) found that most metals do not biomagnify appreciably in aquatic ecosystems, although there is considerable evidence for biomagnification of methylmercury.

In the same review, Kay (1984) concluded that some toxic organics, including PCBs and mirex, tend to biomagnify. DDT, however, shows little evidence for substantial biomagnification in water-breathing biota, although significant biomagnification is seen at higher trophic levels in wildlife such as fish-eating birds. Based on this review, it may be concluded that biomagnification is not dramatic within aquatic food chains and, where it occurs, biomagnification factors between the lowest and highest trophic levels are usually small (less than an order of magnitude).

2.3.4 Biomonitoring Applications

Approaches to biomonitoring of contaminant bioaccumulation from sediments by bottomdwelling organisms include coincident measurement of sediment contaminant concentrations and concentrations in naturally-occurring biota, as well as measurement of tissue concentrations accumulated by introduced animals maintained in a pollution

gradient. Relatively large-bodied freshwater benthic taxa, most notably freshwater mussels, have been favoured in biomonitoring applications. Bioaccumulation in marine and estuarine lamellibranchs has been measured in biomonitoring applications for several years (e.g., Brooks and Rumsby, 1965; Pringle et al., 1968; Kopfler and Mayer, 1969; Bryan, 1973; Romeril, 1974; Schulz-Baldes, 1974; Watling and Watling, 1976), and provided a foundation for the development of comparable biomonitoring systems using freshwater mussels.

Numerous studies have demonstrated general direct relationships between bulk metal concentrations in sediments and tissue concentrations in mussels. As noted earlier, Tessier et al. (1984) used a sequential extraction technique to elucidate the bioavailable fractions of heavy metals to freshwater mussels. In many instances, tissue contaminant levels have been measured in caged mussels held above the sediments, or in natural populations of mussels along a pollution gradient, without relating bioaccumulation to sediment concentrations (Bedford et al., 1968; Anderson, 1977b; Manly and George, 1977; Foster and Bates, 1978; Marquenie, 1981, Kauss et al., 1981; Hartley and Johnston, 1983; Kauss and Hamdy, 1985; Davis and George, 1987; Rice and White, 1987; Servos et al., 1987). Other taxa that have been used in biomonitoring through tissue contaminant determinations include leeches (Metcalfe et al., 1984), snails (Coughtrey and Martin, 1977), oligochaetes (Chapman et al., 1980; McKee et al., 1985; Hart et al., 1986b), and aquatic insects (Nehring, 1976; Anderson, 1977a).

2.4 Review of Benthic Macroinvertebrate Community Structure Data

2.4.1 Use in Water Quality Monitoring

The composition of the benthic fauna has been the most widely used indicator of water and sediment quality because the macroinvertebrates form relatively sedentary communities in the sediments and reflect the character of both the water and the sediment. The benthic fauna respond to gradual and rapid changes in the quality of their environment, and thus provide an indication of quality characteristics over the long-term as well as in the present. The species composition of the benthic community represents the summation of a variety of environmental parameters besides water and sediment quality, including water depth, sediment type, organic matter, temperature and current (e.g., Eriksen, 1966; Mozley and Garcia, 1972; Cole and Weigmann, 1983). These

parameters all serve to produce heterogeneity in benthic communities which must be taken into consideration when interpreting benthic fauna composition. One often overlooked but important factor is temporal variability. The absence of a particular species, especially insect larvae, may be simply a result of a period of its life cycle (post-emergence) rather than of any environmental disturbance.

In a good water quality environment, the benthic macroinvertebrate community usually consists of many species without a dominant species or species group. Discharge of pollutants in sufficient quantities results in marked and easily detected changes in community structure. For example, the disappearance of sensitive species from benthic groups such as Ephemeroptera (mayflies), Trichoptera (caddisflies), and Amphipoda (e.g., Gammarus spp.) occurs with increased organic pollution and resultant low dissolved oxygen concentrations. Concurrently, species tolerant of organic enrichment, especially species of Oligochaeta (worms), such as Limnodrilus hoffmeisteri, L. cervix, Peloscolex multisetosus and Tubifex tubifex, generally increase in abundance until, under conditions of advanced pollution or eutrophication, they form the total benthic community (Cook and Johnson, 1974). If pollution is increased further to sublethal toxic conditions, there is a marked decrease in organism abundance and biomass, and the community is typified by the occurrence of small numbers of a few species. In the most extreme toxic situations, the benthic macroinvertebrate community is absent.

Four approaches are generally available to measure structural responses to environmental perturbation:

- 1. interpretation of indicator species or taxa.
- 2. changes in relative numbers of individuals or taxa,
- 3. derivation of a species diversity or community comparison index, and
- pattern recognition techniques, involving ordination, cluster, multiple regression and/or discriminant analyses.

Most research on alteration of benthic macroinvertebrate community structure is related to trophic (nutrient) or general pollution conditions rather than exposure to specific persistent toxic substances.

Fitchko (1986a) recently completed a review of a number of studies that have evaluated the utility and sensitivity of specific approaches (structural response tests) in defining the effects of general pollution as well as persistent toxic substances on benthic macroinvertebrate community structure. A brief summary of the available methods and their applicability in general pollution and persistent toxic substance studies is provided below, based on the Fitchko (1986a) review. This is followed by a review of studies providing a comparative evaluation of the utility of these methods to measure structural responses.

Indicator Species or Taxa

Certain species of benthic macroinvertebrates can be characterized as water pollution indicators (e.g., Brinkhurst, 1966; Beck, 1977; Hilsenhoff, 1977, 1982). Based on the degree of sensitivity to the extent of pollution conditions, the species are generally classified as pollution-tolerant, facultative and pollution-intolerant.

For example, good water quality is typified by species of such macroinvertebrate taxa as mayflies (Ephemeroptera), caddisflies (Trichoptera) and stoneflies (Plecoptera). In contrast, dominance of the tubificid oligochaete species, <u>L. hoffmeisteri</u> and <u>T. tubifex</u>, has long been recognized as an indication of poor water quality.

A number of qualitative biotic indexes have been developed based on the pollution tolerance of macroinvertebrate taxa (e.g., Beck, 1955; Beak, 1964; Woodiwiss, 1964). The indexes are generally based on a classification of benthic species into a number of groups based on sensitivity to pollution and a scoring of the number of component groups in any sample. These indexes were frequently used in early studies of water pollution.

A number of studies have been undertaken using the indicator species approach to attempt to identify toxic contaminant effects on benthic macroinvertebrates. Moore et al. (1979) and Moore (1979) could not identify an indicator species in a study of benthic communities in Canadian subarctic lakes contaminated by metals (arsenic, mercury, zinc, copper) and cyanide. Similarly, Chapman et al. (1982a) and Chapman and Brinkhurst (1984) reported that, based on exposures of oligochaete communities to cadmium, mercury and other contaminants, the identification of usable oligochaete species assemblages responsive to specific toxicants was not promising.

Changes in Relative Numbers of Individuals or Taxa

A number of measures of pollution status have been developed that take into account changes in relative numbers of individuals or taxa. For example, one pollution categorization system used by a number of investigators (e.g., Krieger, 1984) is based on the numbers of oligochaetes and mayflies/m² such that:

- o "clean" habitat is indicated by < 100 tubificids/m² and >100 mayflies/m²,
- "light" pollution is indicated by 100 to 1,000 tubificids/m² and <100 mayflies/m²,
- o "moderate" pollution is indicated by 1001 to 5,000 tubificids/m², and
- o "heavy" pollution is indicated by > 5,000 tubificids/m².

Goodnight and Whitley (1961) and Goodnight (1973) have used relative abundance of oligochaetes as measures of pollution status, such that <60% oligochaetes is indicative of "good" conditions, 60% to 80% is indicative of "doubtful" conditions, and > 80% is indicative of a high degree of either organic enrichment or industrial pollution.

Brinkhurst et al. (1968) developed a trophic condition index derived from the abundances of chironomid species of known tolerances to the ranges of trophic conditions or organic enrichment, using the formula:

Trophic Condition =
$$\frac{\sum n_1 + 2\sum n_2}{\sum n_0 + \sum n_1 + \sum n_2}$$

where $\sum n_0$ is the total number of individuals of chironomid species known to be intolerant of organic enrichment, $\sum n_1$ is the total number in species characteristic of only slightly enriched areas, and $\sum n_2$ is the number belonging to species which are tolerant of more severe organic pollution.

Howmiller and Scott (1977) developed a system that was based on oligochaete species abundance and composition, and used the formula developed by Brinkhurst et al. (1968), where $\sum n_0$ is the number of individuals in intolerant oligochaete species, $\sum n_1$ is the number in species moderately tolerant of organic enrichment, and $\sum n_2$ is the number in tolerant species.

Brinkhurst (1967) suggested that the percentage contribution of <u>L. hoffmeisteri</u> to total oligochaete abundances may be a useful indicator of organic pollution, with higher values indicative of greater organic enrichment.

Several investigators have reported the utility of relative or total abundance of benthic macroinvertebrates in delineating contamination by toxic contaminants. Kansanen and Aho (1981) reported that the scarcity of oligochaetes and Chaoborus flavicans in Karjenniemenselka basin of Lake Vanajaves in southern Finalnd was likely due to high concentrations of zinc in the water and sediments. Aston (1973) reported that heavy metals, such as copper, are likely to eliminate tubificids, but the insecticide BHC may cause an increase in tubificid numbers, whereas other benthic taxa may be eliminated. Gilderhus (1966) reported that average numbers of benthic organisms in experimental pools with the highest arsenic treatment levels were decreased by over 50% compared with average numbers in the controls. Winner et al. (1975) concluded that number of species was the most sensitive index of the impact of copper on a macroinvertebrate community in an experimentally-polluted stream. Finally, Moore (1979) reported a strong negative correlation between the concentration of metals (As, Cu, Pb, Hg, Zn) and the abundance of benthic organisms, suggesting that total density provides a useful measure of the level of contamination.

Species Diversity or Community Comparison Indexes

Since the initial study by Wilhm and Dorris (1968), the use of species diversity and community comparison indexes in the quantitative assessment of water pollution impact on aquatic community structure has been commonplace. The number of biological indexes used to assess water quality has increased constantly and many have been reviewed by various authors (e.g., Peet, 1974; Perkins, 1983).

In theory, assuming all factors in two aquatic environments are equivalent with the exception of their pollution status, the community affected by greater pollution should have a lower species diversity. Some indexes, e.g., Shannon's, include an evenness factor, whereby individuals in the more polluted environment should be less evenly distributed among the species.

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Community comparison indexes have recently received more frequent use in studies of pollution impact on community structure. In theory, if one community is more polluted than another community, then a comparison of the two communities should not be similar with respect to species composition. All other factors being equivalent, their similarity should decrease as pollution increases in one of the communities.

A number of studies have used species diversity indexes to measure community-level stress from persistent toxic substances. Many of these are described in Section 2.4.2. However, Moore (1979) reported that diversity indexes were ineffective in monitoring metal contamination in Yellowknife Bay, Great Slave Lake in the Northwest Territories.

Statistical Techniques

Statistical techniques, particularly pattern recognition techniques such as reciprocal averaging ordination and discriminant analysis, have been used only recently to identify the environmental factors controlling species composition. These techniques can also be used to determine the more specific underlying causes of pollution stress and the consequences on community structure.

Only a few studies have applied sophisticated statistical analyses to the response of benthic community structure to specific toxic contaminants. Ramusino et al. (1981) reported that, based on discriminant analyses, decreases in the numbers of six species of Ephemeroptera in a pre-alpine watercourse in Italy were related to high concentrations of dissolved hexavalent chromium. Other physicochemical variations did not seem to be involved. Using a multivariate comparison, Lang and Lang-Dobler (1979) identified six groups of benthic invertebrate species characterized by a high value of one of ten chemical (eight metals, total phosphorus, organic carbon) variables analyzed. These were:

- Peloscolex ferox, Potamothrix hammoniensis, Limnodrilus claparedeanus and cadmium;
- Psammoryctides barbatus and zinc;
- 3. <u>L. hoffmeisteri, L. udekemianus, L. profundicola</u> and total phosphorus;
- Potamothrix heuscheri, Aulodrilus pluriseta, A. limnobius, Tubifex tubifex, Ilyodrilus templetoni, Stylodrilus heringianus and organic carbon;

- 5. Potamothrix vejdovskyi and mercury; and
- 6. Peloscolex velutinus, S. lemani and manganese.

Pollution level of the sediment decreased from Group 1 to Group 6, so that each of these groups could be used to define a different level of contamination.

BEAK typically uses statistical analysis to relate benthic community parameters to environmental (sediment and water) quality parameters, including simple correlations, multiple regression, cluster analyses and discriminant analyses (Crowther and Luoma, 1984; IEC BEAK, 1985, McKee et al., 1985; Hart et al., 1986b). In a standard statistical application, a sequential ranking procedure (Orloci, 1978) is sometimes used for variable selection. This procedure eliminates redundant variables to produce the smallest possible subset of variables containing a specified percentage of the informtion in the total data set. Logarithmic or angular data transformations are generally required to normalize the data prior to these statistical analyses (Elliot, 1971).

Sample stations are grouped into clusters of similar stations on the basis of either species composition (biological clusters) or physical-chemical characteristics (physical-chemical clusters). Green (1979) discusses cluster techniques with specific reference to detection of meaningful patterns in the benthic macroinvertebrate community.

Discriminant analyses are then used to relate the station clusters versus physical-chemical gradients in the environment. Applied to physical-chemical clusters, discriminant analysis defines the combination of parameters which make the station clusters distinct from each other. Applied to biological clusters, the analysis defines the physical-chemical properties associated with differences in species composition and abundance between station clusters. Non-normal physical - chemical variables are transformed prior to analysis. Green (1979) discusses the use of this technique in relating clusters of benthic sampling stations to environmental gradients.

Applying this methodology to pollution studies, a "pollution species assemblage" will be identified which is represented only in the impact portion of the study area and is separated from the other species assemblage groups by a discriminant function with high coefficients only on the "pollutant" variables (Green and Vascotto, 1978).

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Comparative Evaluation of Structural Response Test Utility

A number of studies have evaluated the utility and sensitivity of various structural response tests in defining the effects of general pollution as well as persistent toxic substances on benthic macroinvertebrate community structure. These are discussed below.

A large number of species have been identified as indicators of water quality and general (organic) pollution conditions, e.g., <u>L. hoffmeisteri</u> and <u>T. tubifex</u>. However, the use of particular indicator species, perhaps based on species-specific sensitivity or adaptive potential, or the use of a particular community structure or composition index to delineate detrimental impact on the benthic macroinvertebrate community due to a specific persistent toxic contaminant or contaminant class, was generally not found in the literature (Fitchko, 1986a).

As discussed previously, Moore et al. (1979) and Moore (1979) could not identify an indicator species in a study of benthic communities in Canadian subarctic lakes contaminated by metals and cyanide. Similarly, Chapman et al. (1982a) and Chapman and Brinkhurst (1984) reported that the identification of oligochaete species responsive to specific toxicants was not promising. However, Surber (1959) reported that C. bicinctus had outstanding resistance to chemical pollution, particularly electroplating wastes containing hexavalent chromium, cyanides and copper.

Qualitative (e.g., biotic indexes) and quantitative (e.g., species diversity indexes) measures are sensitive to different aspects of benthic community structure, and therefore are affected differentially by environmental perturbations such as pollution.

Krieger (1984) applied four structural response measures in an evaluation of a benthic data base for the southern nearshore zone of the central basin of Lake Erie. These were: number of oligochaetes/m², relative abundance of oligochaetes, trophic condition index and the percentage of <u>L. hoffmeisteri</u> to total oligochaete abundance. The abundance and relative contribution of oligochaetes as well as oligochaete trophic condition index showed significant differences between the polluted harbours and the less polluted open waters of nearshore Lake Erie. The relative contribution of <u>L. hoffmeisteri</u> and the trophic condition index based on chironomids failed to demonstrate

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a difference between the harbours and open areas. The indexes based on absolute and relative abundances of oligochaetes suffered however from their inability to detect subtle changes in pollution which may not affect overall oligochaete abundances, but which may cause changes in species composition due to different functional responses of species populations.

In a study of the distribution of oligochaetes in Lake Michigan, Lauritsen et al. (1985) compared three methods using oligochaete data to assess water quality: relative abundance of Stylodrilus heringianus (high values indicate little organic enrichment), the percentage of L. hoffmeisteri to total oligochaete abundance, and trophic condition index. The methods showed similar patterns, indicating that southern Green Bay and parts of the southern and northern basins of the lake are organically enriched environments. However, because the structural response measures do not take into account the complex interactions between biotic and abiotic factors, they cannot be used to predict precisely the responses of oligochaete species in situ to specific environmental conditions or toxins.

In a study of the effect of sediment copper on the distribution of benthic macroinvertebrates in the Keweenaw Waterway, Kraft and Sypniewski (1981) found that equitability and Shannon-Weiner diversity values did not indicate pollution because of the extremely low and thus even numbers of individuals collected in all taxa. In the unpolluted areas, Hexagenia, Peloscolex and Pontoporeia were often abundant, producing considerable unevenness in the number of individuals in the various taxa. In the polluted area where the three pollution-intolerant taxa were generally absent, the few taxa present were each represented by a very few individuals, producing a high degree of evenness in the numbers of individuals in the various taxa. As a result, ten of 15 polluted sampling locations had diversity values above 2.5. Moreover, six polluted stations had higher diversity values than the 15 unpolluted stations, even though these polluted stations only had an average of 57% of the number of taxa. In the case of equitability values, Weber (1973) reported that even slight levels of pollution reduce the values to below 0.5 and often below 0.3. However, 13 of the 15 polluted stations had values above 0.5. Of these 13 stations, eight stations were above 0.7, whereas three stations were above 0.9. Based on these results, it was concluded that the Shannon-Weiner diversity and equitability indexes were grossly inadequate as measures of heavy metal pollution.

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Several studies have been undertaken involving community structure bioassays to assess the toxicity of a persistent toxic substance using the Shannon diversity index or other indexes. Based on experimental exposure of a stream benthic community to chronic copper stress, Winner et al. (1975) reported that simple measures of community structure, such as number of individuals and number of species, were more strongly and more significantly correlated with copper concentrations than either the Margalef or Shannon diversity index. The number of species was the most sensitive index of the impact of copper on macroinvertebrate community structure.

Perkins (1983) evaluated the adequacy of 13 indexes in assessing the structural response of a benthic community to geometric increase in copper concentration in experimental streams. The Shannon diversity index was found to be an unreliable measure of structural response to copper stress. Increases in Shannon index values occurred due to decreases in the abundance of several dominant species, or increases in abundance of several rare species resulting from possible enrichment by a low-level perturbation. In contrast, the results of the study suggested that community comparison indexes could be used to indicate even slight impact, i.e., at the lowest copper concentration (0.08 mg/L) used. However, this study did not show that one or even a combination of indexes could accurately indicate the magnitude of impact on the community. Only qualitative estimates of impact magnitude, e.g., low, medium and high impact categorization, seemed possible based on the use of several community comparison indexes.

Using acute toxicity tests, Slooff (1983b) determined the susceptibility of invertebrate species of 13 different taxonomic groups to 15 chemical components and to a mixture of organics concentrated from the Rhine River. The results indicated that the tolerances of macroinvertebrate species are pollutant-specific, whereas the differences within susceptibility to toxic conditions due to contamination by several toxicants may be negligibly small. Therefore, the reliability of using the distribution of benthic organism assemblages as indicators to classify surface waters polluted with a variety of chemical pollutants should be seriously doubted. Only when a waterbody is polluted by a few known toxicants may biotic indices be workable, if they are based on extensive correlations between species presence and water quality and include faunal associations with habitats. Such an approach is data intensive and requires complex statistics and may not be applicable to a waterbody that receives thousands of chemicals of mostly unknown origin.

The data intensive, statistical approach involving pattern recognition techniques is perhaps the most useful method for the identification and assessment of the specific persistent toxic substances having an effect on community structure. Green and Vascotto (1978) critically reviewed the analysis methods which reduce biological data such as species abundances to a more usable form, including ordination, classification and diversity index methods as well as those which relate these reduced data to environmental data. They concluded that classification (or cluster) analysis of the biological data followed by multiple discriminant analysis of the species-assemblage groups on the environmental (including contaminant) variables was the most robust and efficacious procedure.

2.4.2 Extent of the Database

Numerous studies have been undertaken that relate specific contaminant concentrations in sediments to benthic macroinvertebrate community structure. These are listed in Table 2.19. A description of most of these studies is provided below.

The actual sediment contaminant concentration and benthic macroinvertebrate community structure data from some of these studies have been tabulated into a spreadsheet format. Examples of this database are presented in Appendices 1 and 3.

Great Lakes Studies

Rich deposits of copper in the Keweenaw Peninsula area of Lake Superior were mined commercially until 1968, and created extensive deposits of copper tailings in and around the area's lakes and rivers. Huge deposits are located at Freda and Redridge, 20 km from the northern entrance of the Keweenaw Waterway where an estimated 45 million tonnes of tailings were discharged into Lake Superior (Malueg et al., 1984a). Extensive deposits of tailings are also located along the waterway in the Hancock-Houghton area.

A number of studies have been undertaken to assess the effects of copper contamination in the Keweenaw Peninsula area on benthic community structure. For example, Kraft (1979) reported that 42 km² of a 540 km² study area investigated in a nearshore zone of Lake Superior from Freda to the North Entry of the Keweenaw Waterway was devoid of Ponteporeia hoyi. Moreover, there was a reduction in density of this amphipod in the

TABLE 2.19: STUDIES RELATING SPECIFIC CONTAMINANTS TO BENTHIC MACROINVERTEBRATE COMMUNITY STRUCTURE

Contaminant	Reference*			
As	Gilderhus (1966)			
As, Cd, Cu, Ni, Pb, Zn, PCB	JBF (1978)*			
As, Cd, Cr, Cu, Pb, Hg, Ni, Zn	Falk <u>et al.</u> (1973)			
As, Cd, Cr, Cu, Fe, Pb, Hg, Zn, DDT, mirex, PCBs	MOE (1981)*			
As, Cu, Pb, Hg, Zn	Moore <u>et al.</u> (1979)			
Cd, Cr, Cu, Fe, Pb	Neher and Weisel (1977)			
Cd, Cr, Cu, Fe, Pb, Mn, Ni, Zn	Poulton et al. (1986)			
Cd, Cr, Cu, Ni, Pb, Zn	Creal (1983)			
Cd, Cu, Pb, Zn	Roch <u>et al.</u> (1985)			
Cd, Mn, Hg, Zn	Lang and Lang-Dobler (1979)			
Cd, Hg	Chapman et al. (1982a), Chapman and Brinkhurst (1984)			
Cd, Fe, Mn, Ni, Zn	Occhiogrosso et al. (1979)			
Cd, Cr, Zn	Wentsel <u>et al.</u> (1977c)			
Cr, Cu, Zn	Winner <u>et al.</u> (1980)			
Cr, Zn	Wuycheck (1983)			
Cu	Winner et al. (1975), Kraft (1979)*, Kraft and Sypniewski (1981)*			
Cu, Fe, Pb, Hg, Zn	Griffiths (1978)			
Cu, Pb, Zn	Willis (1985)			
Cu, Ni, PCBs	Creal (1981)			
Fe	Johnson and Matheson (1968), Veal (1968)			
Fe, Pb, Zn	Evans (1980)			

TABLE 2.19: STUDIES RELATING SPECIFIC CONTAMINANTS TO BENTHIC MACROINVERTEBRATE COMMUNITY STRUCTURE

Contaminant	Reference*		
Fe, Zn	Hamdy <u>et al.</u> (1978)		
Zn	Kansanen and Aho (1981)		
Cd, Cr, Fe, Pb, Mn, Ni, Zn, PCB	McKee et al. (1985)*		
Cd, Cr, Cu, Pb, Hg, Ni, Zn	Malueg et al. (1984b)*		
Cd, Cr, Cu, Fe, Pb, Mn, Hg, Ni, Zn	Malueg <u>et al.</u> (1984a)*		
Pb, Hg, Zn, chlordane, DDT, PCB	IEC BEAK (1985)		
As, Cd, Cr, Cu, Fe, Mn, Hg, Ni, Pb, Zn, p,p-DDE, dieldrin, endrin, heptachlor epoxide, PCB	BEAK (1987a)		

^{*} Sediment contaminant concentration and benthic macroinvertebrate community structure data in computer database (see Appendices 1 and 3).

surrounding area, which had been impacted by the dumping between 1895-1968 of 50 million tons of copper tailings containing metallic copper in concentrations averaging 3,750 ug/g. In the area devoid of this amphipod, copper concentrations in the sediments ranged from 395 to 1,310 ug/g, while in the rest of the study area mean concentrations were 14 to 298 ug/g. Copper concentration showed significant negative correlation with P. hoyi density.

Kraft and Sypniewski (1981) investigated the effect of copper contamination in the Keweenaw Waterway on benthic macroinvertebrate distribution. Mean copper concentrations in sediments of the northern and southern portions of the Waterway were significantly different (589 and 33 ug/g, respectively). A reduction was found in the number of taxa (mean of 8.4 versus 19.8) and individuals (mean of 1,304/m² versus 5,543/m²) of benthic macroinvertebrates in the north portion compared to the south portion. Molluscs, crustaceans and mayflies sensitive to copper pollution (Arthur and Leonard, 1970; Winner et al., 1980) were absent or nearly so in the north area, but widespread and abundant in the south area.

Similarly, Malueg et al. (1984a) reported that macroinvertebrate populations and number of taxa were all higher at the southern stations than the northern stations of the Keweenaw Peninsula. Organism numbers and number of taxa averaged $110/m^2$ and 3.8 taxa respectively in the north, and $491/m^2$ and 13.4 taxa respectively in the south. Mean diversity was only 0.38 in the north compared with 0.81 in the south. A positive relationship occurred between copper concentration in the sediments and field distribution of macroinvertebrates. Ephemeroptera were the dominant taxon in the south, but were not collected in the north. Chironomids dominated nearly the entire population (96%) in the north, but accounted for less than 25% of the organisms in the south.

Finally, Malueg et al. (1984b) also reported that Torch Lake, draining into the Keweenaw Waterway, was characterized by low diversity and reduced populations of benthic macroinvertebrates due to high copper concentrations. Sediment that elicited a significant mortality (40,0%) in a laboratory bioassay with H. limbata contained only 14 dipterans/m².

Veal (1968) reported severe impairment of the benthic community due to industrial and municipal discharges to the St. Marys River. No macroinvertebrates were found at locations near an outfall and trunk sewer of a steel plant where iron concentrations in the sediments were 25 and 44%, respectively. Other toxic contaminants identified included oils, phenols, cyanide and naphthalene. Partial recovery occurred through stages beginning with the appearance of one or two oligochaete species, Limnodrilus hoffmeisteri and Tubifix tubifex, followed by a greater variety of pollution-tolerant species including midge larvae, leeches, lumbriculids, enchytraeids and other tubificids, and finally with the appearance of amphipods, isopods, clams and snails adding additional diversity. This disruption of benthic community structure occurred along the Canadian shoreline for at least 4 km downstream. A clean water fauna characterized the relatively unindustrialized U.S. shore and all portions of the river upstream of pollution sources.

In a later study, Hamdy et al. (1978) also reported that the macroinvertebrate community structure in the St. Marys River was severely disrupted due to discharges from the steel mill operations. Severe toxicity, defined by a species diversity of less than 2, number of species less than 4, and benthos abundance less than 100 individuals per m², occurred downstream of the steel plant main trunk sewer outfall and a paper mill outfall. The high concentrations of iron, zinc, cyanide, oil and phenolic compounds likely restricted the survival of most macroinvertebrate species in this zone and drastically reduced the abundance of tolerant species.

More recently, BEAK (1987a) showed that the benthic communities of the St. Marys River in 1983 and 1985 were generally similar to the communities reported in 1968 and 1973. This study examined relationships between sediment quality and benthic communities structure. It was found that the disappearance of burrowing mayfly nymphs coincided with the spread of oil in the bottom sediments, as reported earlier by Hiltunen and Schloesser (1983). Using cluster and discriminant analysis, benthic station clusters identified, based on species composition, were found to be distinguished by discriminant functions having iron, zinc and pesticide concentrations in sediments as key elements, suggesting that these contaminants may be influencing community structure. Similarly, benthic species clusters, or guilds, were identified whose dominance was related by multiple regression to sediment arsenic, chromium, mercury, heptachlor epoxide, clay, total organic carbon and loss on ignition. The two statistical approaches pointed to

different combinations of sediment characteristics as the best multivariate predictors of community structure. Nevertheless, the good agreement between the impact zones defined based on station cluster patterns and species guild dominance patterns confirmed that contamination levels were strongly influencing the benthic community structure.

JBF (1978) reported that oligochaetes (<u>Limnodrilus spiralis</u>, <u>L. hoffmeisteri</u>, and particularly <u>T. tubifex</u>) dominated the benthic macroinvertebrate community on a numerical (9,000 to 215,000/m²; average of 82,000/m²) and percent composition (96.9 to 100.0%) basis in Michigan City Harbor. <u>Procladius</u> sp. dominated the sparse chironomid fauna. Diversity at all stations was very low. The total taxa, which included organisms identified at least to genus, ranged from five to 11. Based on a qualitative comparison, there was no apparent relationship between benthic macroinvertebrate community structure and sediment contaminant concentrations. It would appear that the dominant influence on the benthic macroinvertebrate community was organic pollution, which likely masked any toxic effects exerted by sediment contaminants. Even at locations with relatively lower sediment contaminant concentrations, the benthic assemblages indicated severe organic pollution.

Cook and Veal (1968) reported that the benthic community within the turning basin of Port Hope Harbour was characterized by high numbers of pollution-tolerant species and low diversity. One sampling location near an industrial discharge point was devoid of macroinvertebrates, indicating severe pollution of this part of the basin. impairment was likely due to high concentrations of radionuclides, ammonia, fluoride and such heavy metals as arsenic and nickel. McKee et al. (1985) and Hart et al. (1986b) recently completed an update study of Port Hope Harbour, relating sediment contaminant levels to benthic community structure using cluster and discriminant analyses. Data indicated that densities of benthic organisms were considerably higher on average in 1984 than reported in 1968, and the apparent acute toxic responses noted near the discharge in 1968 were not obvious in 1984. Based on cluster analyses, the turning basin and outer harbour benthic communities were distinctive, with tubificid oligochaetes dominating both communities. The differences could be attributed either to differences in contamination, habitat or both. All contaminants (radionuclides, metals, PCBs) analyzed were higher in concentration in the turning basin than in the outer harbour. The most significant univariate differences occurred for uranium and zinc. Radium-226 made the greatest unique contribution to the overall environmental separation of the two groups of stations.

2369.1 2,78

Johnson and Matheson (1968) reported that no macrobenthic community occurred in Hamilton Harbour sediments containing more than 25% Fe₂O₃. Griffiths (1978) reported that only the amphipod <u>Gammarus fasciatus</u>, seemingly tolerant of the high levels of copper (278 ug/g) in the sediments, was present at an antecedent outfall location of a chemical plant in the St. Lawrence River.

As part of the overall study on impact of Hamilton Harbour on western Lake Ontario, Poulton et al. (1986) examined relationships between benthic macroinvertebrate community structure, water depth, substrate type and sediment concentrations of metals (Cd, Cr, Cu, Fe, Pb, Mn, Ni, Zn). Water depth proved to be the overriding factor in the distribution of benthic organisms and heavy metals in the sediments.

IEC BEAK (1985) undertook a correlation analysis of benthic and physical-chemical sediment parameters to define ecological relationships in the nearshore Toronto waterfront area. The lack of correlation for the open lake stations between three benthic parameters (total densities, number of taxa and percent tubificids) and the concentrations of metals (lead, mercury, zinc) and persistent organic contaminants (PCBs, chlordane, DDT) suggested that these contaminants were not evoking detectable responses in benthic community structure. The embayed stations showed significant correlations between the benthic parameters and a number of sediment quality parameters, e.g., cation exchange capacity, organic carbon, lead, zinc and chlordane. However, the correlations were developed from relatively few data points and may be spurious.

Creal (1981) reported significant reduction of taxa and abundance in the benthic macroinvertebrate community of Little Portage Creek, Michigan, downstream of an industrial effluent discharge with high concentrations of copper and nickel. Wuycheck (1983) also qualitatively related macroinvertebrate community structure (abundance and diversity) to sediment contaminants, e.g., heavy metals, PCBs and cyanide, in the Kalamazon River.

Evans (1980) reported that macroinvertebrate community structure in Monguagon Creek, which discharges to the Trenton Channel of the Detroit River, indicated a degraded to completely degraded stream condition. No macroinvertebrates were found immediately downstream of an unpermitted discharge by a chemical company. Pollution-tolerant

organisms dominated the macroinvertebrate community upstream of the discharge due to the effects of other industrial discharges. Extremely high concentrations of iron (33,000 ug/g), lead (640 ug/g) and zinc (4,700 ug/g) and elevated concentrations of other metals were found in the sediments. Extremely high concentrations (more than 1,000 mg/L) of chlorine may be the most significant toxic contaminant causing biotic extinction.

A number of other studies have been undertaken in the Great Lakes that relate benthic macroinvertebrate community structure to general toxic and/or organic pollution. These have been reviewed recently by Fitchko (1986a).

Other Studies

Malueg et al. (1984b) found no benthic macroinvertebrates at a location receiving the drainage from one of California's most productive copper mines which operated during the first half of this century. Sediment at this location had the highest copper contamination (2,700 ug/g) and elicited 100% mortality in a laboratory bioassay with H. limbata. However, farther downstream, populations increased from 350 and 363 organisms per m² at locations downstream of the mine and tailings to 1,826/m² at a location substantially further downstream. Sediment copper concentrations were 2,000 and 2,200 ug/g at the two locations downstream of the mine and tailings, and 550 ug/g at the location further downstream. Sediments from these three locations elicited high mortality (93.3 to 100.0%) in laboratory bioassays with H. limbata. The number of taxa at these three locations ranged from 18 to 36 compared with 64 taxa at a location above the mine. Sediments from this upstream location elicited low mortality (13.3%) of H. limbata comparable to that in the control bioassay (6.7% mortality).

For the Phillips Chain of Lakes in Wisconsin impacted by a metals plating factory, Malueg et al. (1984b) reported that the benthic macroinvertebrate community at the one location with greatest metal contamination was characterized by few taxa, the least biomass and lowest species diversity. Sediments only from this location elicited toxicity during laboratory bioassay exposures of \underline{D} . Magna. There were only seven taxa of benthic macroinvertebrates at this location and a biomass of 2.24 g/m² dry weight. Species diversity, as expressed by H' and the number of species in the top 75% of the total population, was 0.47 and 1.38, respectively. In contrast, a location farthest from the contaminated area was characterized by 12 taxa, a biomass of 12.03 g/m² dry weight, an H' diversity of 0.89 and 3.98 species in the top 75% of the population.

Willis (1985) reported reduced numbers of individuals (234.2) and taxa (14.4) in a drainage system impacted by mine-waste. Concentrations of copper, lead and zinc averaged 1,110, 4,265 and 23,000 ug/g, respectively, in the drainage system sediments. At the discharge of the drainage system to a larger-order stream, the numbers of individuals and taxa increased to 580.6 and 32, respectively. Species diversity (Mangalet's Index) was 2.57. Sediment concentrations of copper, lead and zinc at this location were lower (i.e., 355, 5,010 and 8,200 ug/g, respectively, on average). Species diversity was higher at 4,92. The number of individuals, taxa and species diversity increased additionally at locations progressively downstream to approach those at an upstream control (872.4 individuals, 35.3 taxa and diversity of 5.12). Sediment concentrations of copper, lead and zinc at the control location averaged 200, 690 and 550 ug/g, respectively.

Occhiogrosso et al. (1979) reported decreased benthic macroinvertebrate densities with increasing concentrations of nickel and cadmium in sediments of Foundry Cove in the Hudson River. Only 674 organisms/m² were found at the most highly contaminated location, with sediment cadmium concentrations ranging from 3,450 to 48,100 ug/g and sediment nickel concentrations ranging from 1,700 to 11,400 ug/g. Oligochaete comprised 90% of the benthic community. In contrast, at a location less impacted by metal contamination, 1,759 organisms/m² were found, with oligochaetes and chironomids dominating and occurring in similar proportions. Sediment cadmium and nickel at this location ranged from 20 to 135 ug/g and 46 to 104 ug/g, respectively.

Moore et al. (1979) found that the number of species and total densities were lower in Canadian subarctic lakes contaminated by arsenic, mercury and copper compared to less contaminated lakes further downstream in the drainage system. For example, nine species, comprising a total standing crop of 400 to 860 organisms/m², were found in Meg Lake, which receives wastes from a gold mine. Average sediment concentrations in Meg Lake were 539 ug/g arsenic, 132 ug/g mercury and 477 ug/g copper. The benthic macroinvertebrate community in Keg Lake, downstream of Meg Lake, consisted of 13 species, with total densities ranging from 330 to 1,500 organisms/m². Average sediment concentrations in Keg Lake were 349 ug/g arsenic, 47 ug/g mercury and 544 ug/g copper. Finally, the benthic macroinvertebrate community in Peg Lake, downstream of Keg Lake, comprised 14 species, with total densities exceeding 10,000 organisms/m². Average sediment concentrations in Peg Lake were 76 ug/g arsenic, 80 ug/g mercury and 106 ug/g copper.

2369.1 2.81

Wentsel et al. (1977c) found a significant negative correlation between chironomid numbers and cadmium as well as zinc concentrations in the sediments of Palestine Lake, Indiana. The chironomid C. tentans was absent from areas of highest sediment contamination, i.e., 969 ug/g cadmium, 2,106 ug/g chromium and 14,032 ug/g zinc. However, chironomid numbers increased to an average of 28 individuals per grab sample in the less contaminated area of the lake, i.e., 4 ug/g cadmium, 38.5 ug/g chromium and 139 ug/g zinc. In contrast, specimens of the aquatic oligochaete Limnodrilus sp. were abundant (89/sample) in the most heavily impacted areas of the lake and scarce (3,4/sample) in the unaffected area.

Falk et al. (1973) present concurrent data for benthic community structure (number of individuals and taxa) and metal (As, Cd, Cr, Cu, Pb, Hg, Ni, Zn) concentrations in sediments collected from water bodies affected by mining activities. A cursory examination of this database suggests low benthic macroinvertebrate densities and number of taxa consistently occur in those sediments with the highest metal concentrations.

Winner et al. (1980) reported that in a stream impacted by high concentrations of copper, chromium and zinc in effluent from a small metal-plating industry, macroinvertebrates, other than tubificid worms and chironomids, were virtually eliminated from rock-rubble, riffle habitats. The number of species of chironomids increased from 15 at the most polluted station to 39 at the least polluted stations. The number of species of chironomids was inversely related to the proportional density of the family in samples. Based on a consistent relationship found between intensity of metal stress and the ratio of chironomids to total insects in the benthic community, it was suggested that percentage of chironomids in samples may be a useful index of heavy metal pollution.

Wallace and Brady (1971) reported that immediately downstream of a woolen mill effluent outfall that used dieldrin as a moth-proofing agent, the number of benthic macroinvertebrates was greatly reduced (42/m²), with only oligochaetes and chironomid larvae present. In contrast, the upstream control location was characterized by a significantly larger number of individuals (947/m²) and greater species diversity. At a location further downstream of the outfall, density increased significantly to 6,500+/m², with oligochaetes and particularly chironomids dominating the community. Levels of dieldrin in water and/or sediments were not determined.

2.5 Studies Involving Other Toxic Contaminants

During the literature search, studies on toxicity, chemical release potential, bioaccumulation and benthic community structure effects of other specific contaminants not addressed in this study were identified. These are listed in Table 2.20.

2.6 Workplan A Summary

A comprehensive review of sediment toxicity bioassay methods reveals a large number of different test systems in use, based on benthic organism responses such as acute and chronic toxicity (e.g., <u>Asellus, Hexagenia</u>), avoidance of contaminants (e.g., <u>Pontoporeia, Chironomus</u>), physiological responses (e.g., cilia beat rates of fingernail clams, bacterial bioluminescence) and biochemical responses (e.g., enzyme inhibition or activation). Test media have included sediment-water systems, suspended sediment systems, elutriates, extracts and porewaters. Care must be taken in comparing test results to ensure that similar media and endopoints are compared.

In tests of natural or spiked sediment samples, toxicity has most often been related to heavy metal concentrations (e.g., copper, nickel, lead, iron, chromium, cadmium). Toxicity has been definitively related to persistent organic contaminants only in laboratory tests with spiked sediments (e.g., endrin toxicity to Stylodrilus heringianus). In natural sediments, organic contaminants are frequently below the analytical detection limit, reducing the power of toxicity correlation studies.

Fish embryo-larval mortality has been related to heavy metals in sediments using rainbow trout (<u>Salmo gairdneri</u>) and largemouth bass (<u>Micropterus salmoides</u>). Mercury, cadmium and zinc concentrations have been correlated with embryonic mortality in trout, while cadmium concentrations have been correlated with toxicity to bass embryos.

Teratogenicity has been associated with polluted sediments using both fish embryo-larval systems (e.g., rainbow trout embryonic response to cadmium, mercury and zinc) and insect larvae, particularly chironomids. Insect terata have been linked to specific toxicants only in the laboratory. The large number of contaminants present in polluted environments has generally prevented specific correlation of concentration and response in the field.

Contaminant	Type of Information	Reference	
Permethrin	Toxicity to <u>Hexagenia rigida</u>	Friesen <u>et al.</u> (1983)	
Ba, cyanide	Toxicity to Hexagenia limbata, Asellus communis and Pimephales promelas; concentration in overlying water	Prater and Hoke (1980)	
Sb	Concentration in interstitial water	Brannon and Patrick (1985)	
Al, V	Toxicity to <u>Hexagenia limbata</u> ; benthic macroinvertebrate community structure	Malueg <u>et al.</u> (1984a)	
Sr, V	Toxicity to Hexagenia limbata; benthic macroinvertebrate community structure	Malueg <u>et al.</u> (1984b	
Al, Ba, Be, B, Co, Mo, Ag, Sr, Ti, Y, diazino, dy forate, connel, nethyl parathion, mala thion, ethyl parathion, DEF, ethion, phencaptor, EFN, azimphos methyl, phosalone, azimphos ethyl, coumpaphos, treflan, syrron, azimphos ethyl, coumpaphos, treflan, syrron, azimphos ethyl, coumpaphos, treflan, syrron, azimphos phosin, methoxyethor, 2,4-D iso-proylester, DNEP, endosulfan I, endosulfan II, DEFP, chloroberilate	Toxicity to <u>Menagenia limbata</u> and <u>Atellus</u> <u>communis</u> : concentration in overlying water	Prater and Anderson (1977b	
Ai, Ba, Be, B, Co, Ag, Sn, Ti	Toxicity to Hexagenia limbata and Asellus communis; concentration in overlying water	Prater and Anderson (1977a	
Kepone	Toxicity to three species of oligochaetes	White (1984)	
Co. Se, pentachlorophenol, specific PAH's	Toxicity to <u>Hexagenia limbata</u> ; concentra- tion in overlying and interstitial water; bioconcentration in benthic macroinvertebrates	Bahnick <u>et al.</u> (1981a)	
Octachlorostyrene	Bioconcentration by Lampsilis radiata siliquo.dea	Pugsley <u>et al.</u> (1985)	
Acridine	Bioconcentration by Pimephales promelas	Southworth et al. (1979)	
Specific PAH's	Bioconcentration by chironomids	Eadle et al. (1982a)	
Se	Bioconcentration by benthic faunal groups and fishes	Lemly (1985)	
PAH's	Bioconcentration by Pontoporeia affinis	Eadle <u>et al.</u> (1982b)	
Co	Bioconcentration by <u>Tubifex</u> sp.	Andrews et al. (1985)	
Se, Sn, specific PAH's	Bioconcentration by mussels	Heit <u>et al.</u> (1980)	
Terbutryn, fluridone, TPP, trans-permethrin, methoxychlor	Concentration in overlying water	Muir et al. (1983)	
Al, Ba, Se	Bioconcentration by benthic invertebrates	Guthrie and Cherry (1979)	
Co	Bioconcentration by tubificids	Chapman <u>et al.</u> (1980)	
Se, Cs, Rb, Sb	Bioconcentration by yellow perch	Seelye <u>et al.</u> (1982)	
Al, Ba, Co, Cs, Sb, Se, Ti	Bioconcentration by Enallagma sp., chironomids, Procambarus sp., Libellula sp.		
Se Se	Bioconcentration by channel catfish and smallmouth buffalo	Winger and Andreasen (198.	
Deltamethrin, fenvalerate, cypermethrin, permethrin	Bioconcentration by <u>Chironomus</u> tentans	Muir et al. (1985)	
Co .	Bioconcentration by oligochaetes	Acres (1983)	
Nine chlorobenzenes, hexachloro- butadiene	Bioconcentration by benthic faunal groups	Fox <u>et al.</u> (1983)	
Co, Lı	Bioconcentration by three clam species, tubificids and three bottom-dwelling fish species	Mathis and Cummings (197)	
Co	Benthic invertebrate community structure	Griffiths (1978)	
Fluridone, terbutryn	Bioconcentration by Chironomus tentans	Muir <u>et al.</u> (1982)	
2,3,7,&TCDD, 2,3,7,8-TCDF	Bioconcentration by goldfish	O'Keefe <u>et al.</u> (1986)	
Cypermethrin	Benthic invertebrate community structure	Crossland (1982)	

Contaminant	Type of Information	Reference
Toxaphene	Bioconcentration in benthic faunal groups and fishes	Hannon <u>et al.</u> (1970)
PCDDs, PCDFs	Bioconcentration by carp	Kuehl <u>et al.</u> (1987)
Phenol, cyanide, 2,4-D-isopropyl ester, di-n- butyl phthalate, DCPA, endosulfan 1, endosulfan II, di-2-ethylhexyl phthalate, tetradefon, treflan, zytron, isodrin, o,p-DDE, o,p-DDD, methoxychlor	Toxicity to <u>Hexagenia limbata</u> and fathead minnow	Applied Biology, Inc. (1982)
Ba, phens), cvanide, endosulfan I, endosulfan II, lendssulfan III, endosulfan III, endosulfan III, endosulfan III endosulfan I	е,	ATEC (1983, 1984a, b. 1985c, d. e. 1986a, b. c. d
Ba, As, endosulfan I, endosulfan II, endosulfan sulfate, á -BHC, endrin aldehyde, methoxychlor, toxaphene	Toxicity to <u>Hexagenia limbata</u> and fathead minnow	ATEC (1984c, 1985a, b)
Se, 2,4-D-ispropy leater, dischalti- behalter, DEA (dachal), endouslan I, endouslan II, de-2-eth-jinesy) phthalate, extendaton, tettal (rifluralin), zyron, sodrin, methoxychlor, op-DDD, op-DDE, apphelaiene, aerosphitylene, caronaliberie, riouerene, phramitherene, ambracene, lioueratheren, lioueratheren, benedick liuroantheren, benedick livroantheren, sidenzolalamthracene, benody liberylene, ndemici(1,3-c-dyrene	Toxicity to <u>Hexagenia limbata</u> and <u>Asellus</u> <u>intermedius</u>	Recra (1981)
Cyanide, phenol, ci-n-butyl phthalate, di-2-	Toxicity to fathead minnow	EG&G Bionomics (1983)
butyl phthalate, di-2-ethylhexyl phthalate, o,p-DDE, o,p-DDD, methoxychlor		
butyl phthalate, di-2-ethylhexyl phthalate,	Toxicity to and bioconcentration by four species of benthic macroinvertebrate species and channel catfish	Peddicord <u>et al.</u> (1980)
butyl phthalate, di-2-ethylbexyl phthalate, p,p-DDE, o,p-DDD, methoxychlor	species of benthic macroinvertebrate species	Peddicord <u>et al.</u> (1980) Chapman <u>et al.</u> (1986)

Mutagenicity has generally been determined in sediments using the Ames test with various sediment extracts as media. The test cannot be performed on whole sediments. A sex-linked lethal mutation test with nematodes (Panagrellus) also uses sediment extracts. The Tradescantia stamen hair assay for somatic mutation is well-suited to whole sediment testing, although both contaminant uptake and metabolic activation in the plant system may differ from that in animals.

Neither mutagenicity nor carcinogenicity have been conclusively correlated with specific contaminants in natural sediments, although known mutagens are often isolated from sediments which have tested positive in the Ames test, or where fish with tumours have been collected. Thus, there is considerable circumstantial evidence for a contaminant etiology of fish tumours. The best evidence for correlation of fish tumours with specific contaminants involves hepatic neoplasms in English sole (related to polynuclear aromatic hydrocarbons) and in rock sole (related to metals) in the Puget Sound area. Other neoplasia (e.g., melanoma, papillomas, gonadal) have been widely reported in mainly bottom-dwelling fish (e.g., brown bullhead, white sucker) from polluted locations.

Contaminant sorption capacity is a key factor influencing toxicity of sediments and suspended solids. This, in turn, is related to organic carbon content and particle size. In addition, metal toxicity may depend upon methylation or alkylation by microorganisms (e.g., mercury, arsenic, lead), or on oxidation state (e.g., mercury, chromium). The latter is a function of pH and dissolved oxygen. Physical factors such as dredging and bioturbation, by altering sediment geochemistry and changing the chemical form of contaminants, may modify toxicity directly, as well as mobilize contaminants to the water column.

Bioconcentration of toxic contaminants by aquatic organisms is influenced by many factors, such as local feeding habits, life cycle stage, season and previous exposure history of organisms. Bioconcentration factors for metals tend to approximate unity, although higher values have been reported for zinc, mercury and cadmium than for other metals. Bioconcentration factors for organics are more variable, ranging over several orders of magnitude, although there are fewer organic data. The highest bioconcentration factors reported have been for organic compounds.

Many of the factors influencing toxicity also affect bioaccumulation (e.g., oxidation state of metals, particle size and organic content of sediments). In addition, organic bioaccumulation depends on the lipid content of the organism and the hydrophobicity (or octanol-water partition coefficient) of the contaminant. Competing chemical species can also modify contaminant uptake.

Benthic community structure is necessarily altered by sediment toxicity, since benthic macroinvertebrate species vary in sensitivity. Typically, community diversity is reduced as sensitive species are replaced, and densities initially increase with pollution stress. Most tolerant species can achieve very high densities in the absence of competition. As toxic thresholds of tolerant organisms are approached, total organism density declines with increasing contaminant concentration.

Various indices, in addition to total density and diversity, have been devised to express these community changes quantitatively. Densities of particular indicator species (e.g., <u>Tubifex</u> in lacustrine systems), trophic condition indexes (based on chironomids or oligochaetes), and dominance indexes for groups of tolerant taxa all have been related to toxic contaminants, particularly heavy metals. Pattern recognition techniques are quite useful in identifying natural groups of taxa (based on distribution) or groups of sampling stations (based on species present). These groupings tend to be associated with pollution inputs if pollution is an important factor shaping community structure.

3.0 WORK PLAN B - IN-PLACE POLLUTANTS PROGRAM DATA ANALYSIS

3.1 Tissue Concentration-Sediment Quality Relationships

Early work has shown that total body content of trace metals and organics in benthic biota does not correlate well with bulk sediment concentrations of these chemicals. Workers have, therefore, examined various chemical properties of the sediments and the chemical partitioning of contaminants within the sediments with the aim of finding relatively simple "universal predictors" of the body burden of these chemicals in benthic biota. These "universal predictors" may consist of:

- for metals, contaminant concentrations in particular chemical fraction(s)
 of the sediments identified as source fractions for contaminant uptake by
 benthic macroinvertebrates and bottom-feeding fish; or
- for organic contaminants, bulk sediment concentrations of contaminants taking into account modifying properties of both the sediments and the biota.

Following the first approach, attempts have been made to correlate the heavy metal contents of deposit-feeding macrofauna with operationally defined chemical fraction(s) of the metal in the sediments (Luoma and Jenne, 1976; Bryan and Hummerstone, 1977; Bryan and Uysal, 1978; Luoma and Bryan, 1978; Luoma, 1983; Tessier et al., 1984). Thus Luoma and Bryan (1978) related the lead content of the bivalve Scrobicularia in an estuary in Britain to the ratio of lead/iron in the sediments extracted with 0.1 N HCl. Zinc content of Scrobicularia was related to easily-exchangeable zinc in the sediments (Luoma and Bryan, 1979). In the same study, the zinc content of the bivalve Macoma balthica from San Francisco Bay was related to the oxide-bound iron divided by easily exchangeable manganese and organic carbon in the sediments. Tessier et al. (1984) related the copper concentration in the bivalve Elliptio (a filter feeder) to the ratio of copper (exchangeable + carbonate-bound + iron/ manganese oxide-bound) to oxide-bound iron in freshwater sediments.

The assumption behind the chemical fractionation approach is that metal uptake by the benthic organism is selective for certain fractions, and that contaminants in other fractions are primarily unavailable. Thus, contaminant concentrations in the available

fractions should be most strongly correlated with concentrations in tissues. Recently, a radiolabelling technique has been devised to directly identify the bioavailable chemical fractions in sediments. Andrews et al. (1985) used this approach to identify the easily-exchangeable fraction as the most probable source of cobalt for <u>Tubifex</u> worms fed on natural Ottawa River sediments. More recent work on Toronto Harbour sediments suggests that zinc bound to iron and manganese oxides constitutes the primary source for uptake by Tubifex and Limnodrilus (BEAK, 1987b).

The uptake of organic contaminants in sediments has been related experimentally to a variety of factors, including the chemical structure of the contaminant (Goerke et al., 1979), its degree of hydrophobicity (Neely et al., 1974; Chiou et al., 1977; Veith et al., 1979; Oliver, 1984), the size of the organism (McLeese et al., 1980), its lipid content (McFarland, 1984), the duration of exposure (McLeese et al., 1980), the bulk sediment concentration of contaminants (Fowler et al., 1978) and sediment characteristics such as organic content and particle size (Lynch and Johnson, 1982). Most of these factors influence partitioning of the contaminant between the organic fraction of the sediments and the lipid fraction of the organism. A simple equilibrium partitioning model has been proposed by McFarland (1984) and Rubinstein and Lake (1986):

$$C/I = K \frac{C_s}{f_{\infty}}$$

where: C is the concentration in the whole organism.

I is the lipid fraction,

Cs is the whole sediment concentration,

 f_{oc} is the organic carbon fraction of the sediments, and

K is a constant.

C/I represents a bioaccumulation potential, the maximum concentration of an organic compound that could be accumulated by an organism consisting entirely of lipid tissues.

In order to develop useful models for predicting the body burden of metal and organic compounds in benthic organisms, a number of different models were tested in the study using MOE chemical data from the In-Place Pollutants Program. As part of this program, samples of sediments and various benthic organisms, primarily Oligochaeta and sculpins of several species, have been collected and analyzed for metals and organics since 1983 or 1984 in different areas of concern around the Great Lakes. The modelling approaches used for metals and organic contaminants differ substantially, and are separately described in the following sections.

3.1.1 Heavy Metal Relationships

Sediment samples which had been subjected to fractionation were matched with benthic tissue samples from the same dates and locations, in order to determine correlations between heavy metal concentrations in tissue and concentrations in either bulk sediments or individual fractions. The fractionation scheme was as follows:

IW = Interstitial Water

F1 = Cation Exchangeable Fraction F2 = Easily Reducible Fraction

F3 = Organic Complex F4 = Fe/Mn Hydroxides

Residual = Residual Phase

The fractionation and chemical analyses were performed on the fine particulate component of the sediments (<63 u).

Some samples of bottom water overlying the sediment samples (1 m above the bottom) were also examined for correlations between metal concentrations in water and concentrations in bulk sediments or individual fractions. All concentrations reported as 'less than' detection in either water, tissue or sediment were considered to be equal to one-half the detection limit for purposes of statistical analysis.

Tissue and sediment concentrations in the database which were not already expressed on a dry weight basis were converted to a dry weight basis using the following conversion factor:

$$C_{dry} = \frac{C_{wet} \cdot 100}{100 - \% \text{ loss on drying}}$$

Tissue concentrations corrected in this way were also corrected for gut contents as follows:

$$\frac{C_{\text{gut corrected}}}{100} = \frac{C_{\text{dry}} - C_{\text{sed}}}{100} \frac{(\% \text{ ash})}{100}$$

$$\frac{1 - \% \text{ ash}}{100}$$

where: C_{dry} = contaminant concentration in whole organism on dry weight basis.

Cwet = concentration in whole organism on wet weight basis,

C_{sed} = bulk concentration in sediment, and

C_{gut corrected} = concentration in organism tissues excluding gut contents.

Thus, prior to statitical analysis, consistency in basis of expression among samples was ensured.

The gut correction assumes that the gut contents have the same contaminant concentration as the sediment, and that the ash content of the organism is entirely contained in the gut. These assumptions are probably realized, at least approximately, in oligochaetes, and are reasonable for other detritivores. However, they may be problematic in sculpins which are carnivorous and contain considerable ash in their own boney tissues. The correction procedure was applied to fish in the absence of empirical data on purged or gutted samples.

Loss on drying has been experimentally determined in oligochaetes (Howmiller and Scott, 1977) to be 84.1%. Recent unpublished information for sculpins from the MOE suggests a value of 75.8%. These values were utilized in separate correlation analyses with oligochaetes and sculpins (<u>S. bairdi</u>), respectively. Age classes are recorded in the database for some of the sculpin samples, but were pooled to form the sculpin data set.

Correlation analysis was also performed on a combined data set including all benthic samples regardless of taxon. For these analyses, loss on drying was uniformly assumed to be 80%. Ash contents were measured values specific to each sample.

Correlations between bottom water concentrations of heavy metals and concentrations in bulk sediments or fractions are shown in Table 3.1. Good correlations with Interstitial Water (IW) were obtained for copper, arsenic, manganese and nickel. In addition, nickel was positively correlated with the Easily Reducible fraction (F2), and manganese was broadly correlated with most fractions and with the bulk sediment determination. Iron in bottom water was positively correlated with the Easily Reducible fraction (F2) and the Fe/Mn Hydroxide fraction (F4).

Correlations between tissue concentrations of heavy metals and concentrations in bulk sediments or fractions are shown in Table 3.2. These correlations were generally lower than those which characterized bottom water (above). Based on the mixed taxa data set, copper in tissues was positively correlated with Interstitial Water (IW) and Fe/Mn Hydroxide (F4) concentrations. Iron in tissues was positively correlated with the Easily Reducible fraction (F2). Arsenic in tissues was positively correlated with the bulk sediment and Organic Complex (F3) concentrations. Manganese in tissues was positively correlated with the Fe/Mn Hydroxide (F4) concentration.

Comparison of the oligochaetes and sculpins in Table 3.2 suggests considerable differences between taxa in patterns of correlation between tissue and sediment concentrations. These are the only two taxa for which adequate numbers of appropriate samples are present in the database. While statistical power is reduced in the taxon-specific data sets, it appears that prediction of tissue concentrations from concentrations in sediment fractions may be possible for some metals (copper, cadmium, iron, arsenic and nickel in oligochaetes; iron, lead, arsenic and manganese in sculpins). Results were not promising for chromium or zinc.

More complex relationships to ratios or sums of several sediment fractions have not been investigated. Possibly, predictive power could be increased by use of more complex predictive functions; however, interpretation of uptake mechanisms underlying such multivariate relationships becomes more difficult.

TABLE 3.1: SIMPLE CORRELATIONS OF BOTTOM WATER CONCENTRATIONS
WITH SEDIMENT FRACTION CONCENTRATIONS OF HEAVY METALS

Heavy	Ge∞hemical Fraction ¹						_
Metal	IW	F1	F2	F3	F4	Residual	Bulk ²
Copper	0.7664*	-0.6023	-0.5929	-0.5739	0.2582	-0.2113	-0.4953
Chromium	0.5029	0.5047	-0.4574	0.0937	0.1461	0.4350	0.1973
Cadmium	-0.1180	-0.4650	-0.2503	-0.1196	-0.1185	-0.1183	-0.1618
Iron	0.3840	-0.3151	0.6368*	-0.6767*	0.7841*	0.1479	0.2968
Lead	0.1642	-0.2090	-0.1310	-0,2763	-0.1070	0.1262	-0.3594
Zinc	0.1981	0.5229	0.1095	-0.3263	0.1268	0.2182	-0.1496
Arsenic	0.9024*	0.1613	0.4447	-0.3485	0.2158	0.1085	-0.2879
Manganese	0.8041*	0.6936*	0.8104*	-0.3346	0.6471*	0.2494	0.6317
Nickel	0.7715*	0.4229	0.6800*	-0,7777	0,2295	0.4218	0.1810

¹ Geochemical Fractions:

IW = Interstitial Water

F1 = Cation Exchangeable Fraction

F2 = Easily Reducible Fraction

F3 = Organic Complex F4 = Fe/Mn Hydroxides

Residual = Residual Phase

² Bulk determination is measured rather than calculated as a sum of fraction concentrations.

^{*} Indicates statistical (not geochemical) significance of correlation coefficient (p<0.001).

TABLE 3.2: SIMPLE CORRELATIONS OF BENTHIC TISSUE CONCENTRATIONS WITH SEDIMENT FRACTION CONCENTRATIONS OF HEAVY METALS

			Geoche	emical Fra	ction l		
Heavy Metal	IW	F1	F2	F3	F4	Residual	Bulk ²
Mixed Taxa							
Copper Chromium Cadmium Iron Lead Zinc Arsenic Manganese Nickel	0.3766* -0.1168 -0.2423 0.0618 -0.0855 -0.1037 -0.0347 0.0314 0.1799	0,0072 -0,1712 -0,1394 0,0973 0,0961 -0,1053 0,0565 0,0688 0,0068	0.2515 0.2247 -0.2877* 0.2981* -0.1590 -0.1136 -0.0295 0.1173 -0.3424	-0.0963 0.1178 -0.2729 0.2547 0.1833 -0.0181 0.3244* -0.0921 -0.3429	0.3025 -0.0386 -0.2127 0.1905 -0.2095 0.0399 0.1036 0.3988* -0.3787	-0.0850 -0.2630 -0.3539* -0.3685* 0.1526 0.1073 0.0707 0.0009 -0.3101	0.0806 0.0129 -0.3057 -0.1672 0.0479 -0.0597 0.3866 0.1116 -0.3812
Oligochaeta							
Copper Chromium Cadmium Iron Lead Zinc Arsenic Manganese Nickel	0.5272* -0.1037 -0.4279 -0.132 -0.0812 -0.0769 -0.2458 -0.0267 -0.0902	0.0821 -0.2662 -0.0999 -0.0669 0.1869 -0.2806 0.1338 -0.1213 -0.4198	0.4135 0.4561 -0.4044 0.2224 -0.2651 -0.2817 -0.2659 -0.1000 -0.6922	0.0265 0.3506 -0.3571 0.4900* 0.4048 -0.1620 0.6223* -0.0860 -0.1586	0.2735 -0.2216 -0.4872* -0.1096 -0.3485 0.0769 -0.1704 0.3658 -0.2654	-0.2894 -0.1180 -0.6414* -0.3236 0.2099 0.0662 -0.2208 0.0758 -0.1482	0.2875 0.2923 -0.4234 -0.1006 0.2026 -0.2915 0.5532 0.0699
S. bairdi							
Copper Chromium Cadmium Iron Lead Zinc Arsenic Manganese Nickel	0.1483 -0.1058 0.2023 0.1770 -0.2795 0.2693 -0.0197 0.1004 0.0569	0.3547 0.1898 -0.2351 0.3366 -0.2301 -0.2438 0.1484 -0.4748 0.1394	0.2751 -0.3420 -0.1598 -0.7515* 0.7001* 0.0021 0.6074* -0.0835 -0.4050	0.1100 0.3051 - -0.6722* -0.0753 0.2571 -0.1870 0.6557* -0.2796	0.3799 -0.1621 -0.3112 0.3154 -0.4835 0.1860 -0.2248	-0.0298 -0.0568 -0.7208* -0.0702 0.3856 0.1094 -0.0865 -0.1194	0.0945 0.2303 -0.2627 -0.7298 -0.0833 0.2885 -0.0900 0.3884 -0.2628

 $[\]frac{1}{2}$ Geochemical Fractions as in Table 3.1, Bulk determination is measured rather than calculated as a sum of fraction concentrations.

^{*} Indicates statistical (not biological) significance of correlation coefficient (p < 0.01).

⁻ Coefficient not computed due to lack of variation in sediment or tissue.

3.1.2 Organic Contaminant Relationships

Pesticide and PCB data were examined for benthic tissue-sediment quality relationships by simple correlation analysis, and by fitting several modified versions of the McFarland-Rubinstein model. In its most complex form, the model was as follows:

$$C/I = b_1 \frac{C_s}{f_{oc}} P_s + b_2 \frac{C_s}{SE}$$

where: C is the contaminant concentration in the whole organism (ug/g),

I is the lipid fraction,

 C_s is the bulk sediment concentration (ng/g),

 $f_{\rm oc}$ is the organic carbon fraction (TOC) of the sediments,

Pe is the silt + clay fraction of the sediments,

b₁ is a constant,

SE is the concentation of solvent extractibles (mg/g), and

b₂ is a constant.

In an alternate version of this model, the particle size variable P_{S} (silt + clay) was excluded.

The model is a multiple regression equation constrained through the origin. Least squares estimates of b_1 and b_2 were obtained using the SPSS/PC+ statistical package (Norusis, 1986). The magnitude of each coefficient depends, in part, on the units of measurement of the variables. However, the coefficients can be standardized to reflect the relative importance of the two terms in the equation. The squared multiple correlation coefficient (\mathbb{R}^2) was computed to represent the predictive power of the complete equation on a scale from 0 (no prediction) to 1 (perfect prediction).

Bulk sediment concentrations were expressed on a dry weight basis in the database. Concentrations in benthic organisms were expressed on a wet weight basis in the database and corrected for moisture and gut contents prior to analysis. Correction factors were as follows:

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$$C_{dry} = \frac{C_{wet} \cdot 100}{100 - \% \text{ loss on drying}}$$

$$C_{gut \text{ corrected}} = \frac{C_{dry} \cdot C_{sed}}{100} \cdot \frac{(\% \text{ ash})}{100}$$

$$= \frac{1 - \% \text{ ash}}{1 \cdot 200}$$

where: C_{dry} = contaminant concentration in whole organism on dry weight basis.

Cwet = concentration in whole organism on wet weight basis,

C_{sed} = bulk concentration in sediment, and

C_{gut corrected} = concentration in organism tissues excluding gut contents.

The gut correction assumes that the gut contents have the same contaminant concentration as the sediment, and that the ash content of the organism is entirely contained in the gut. These assumptions are probably realized, at least approximately, in oligochaetes, and are reasonable for other detritivores. However, they may be problematic in sculpins which are carnivorous and contain considerable ash in their own boney tissues. The correction procedure was applied to fish in the absence of empirical data on purged or gutted samples.

Loss on drying has been experimentally determined in oligochaetes (Howmiller and Scott, 1977) to be 84.1%. Recent unpublished information for sculpins from the MOE suggests a value of 75.8%. These values were utilized in separate model testing with oligochaetes and sculpins (S. bairdi), respectively. Age classes are recorded in the database for some of the sculpin samples, but were pooled to form the sculpin data set.

Model testing was also performed on a combined data set including all benthic samples regardless of taxon. For these analyses, loss on drying was uniformly assumed to be 80%. Ash contents were measured values specific to each sample. Much of the organic contaminant data for sediment or tissue was 'less than detection'. In these cases, the concentration was assumed to be equal to one-half the detection limit.

Prior to testing of the modified McFarland-Rubinstein model, simple correlations of corrected tissue concentrations with corresponding sediment concentrations were determined. Contaminant concentrations were not normalized by lipid or TOC concentration for this analysis. The correlation coefficients are listed in Appendix 4, Table A4.1. Only two significant (p < 0.01) correlations between tissue and sediment concentrations of the same contaminant were found, for PCB (r = 0.41) and HCB (r = 0.64). These coefficients are based on the combined data set including various benthic data. Separate analysis of oligochaete and sculpin data sets revealed a significant tissue-sediment correlation for PCB in oligochaetes (r = 0.42) and for HCB in sculpins (r = 0.77).

These results suggest poor correlations, in general, between tissue and sediment concentrations of organic contaminants when lipid contents of tissues and TOC contents of sediments are ignored.

Two versions of the modified McFarland-Rubinstein model were tested, one with a particle size factor (% silt + clay) in the first term of the equation (Model 2) and one without this factor (Model 1). Performances of these models are compared with respect to \mathbb{R}^2 (the proportion of variation in bioaccumulation potential explained by sediment characteristics), and the standard partial regression coefficients b_1 and b_2 in Appendix Table A4.2. In general, there was little difference in performance of the two models, Model 1 performing better in some cases (e.g., aldrin, endosulphan 1) and Model 2 in other cases (e.g., DMDT, p,p-DDT). Consequently, the simpler model (No. 1) is preferred. Results with this model are summarized in Table 3.3 for Oligochaeta, <u>S. bairdi</u>, and the mixed taxa data set.

For most organic contaminants, the first term of the model, which normalizes sediment concentration by TOC, is the only important contributing term. Therefore, the model could be simplified to its original form with little loss of predictive power. Significant prediction of bioaccumulation potential was achieved (p < 0.05) for all compounds tested, except γ -BHC, DMDT (methoxychlor), endrin and p,p-DDT, using the full mixed tax data ∞ t. However, differences between taxa were apparent. The behaviour of β -BHC, γ -chlordane, heptachlor and mirex fit the model for oligochaetes but not sculpins, while aldrin, DMDT, endosulphan I and II, endrin, endosulphan SO_4 , heptachlor epoxide, oxychlordane, p,p-DDE, p,p-DDT and HCB fit the model for sculpins but not oligochaetes. Five compounds (α -BHC, α -chlordane, dieldrin, PCB and p,p-DDD) fit the model for both oligochaetes and sculpins.

		Oligochae ta			S. bairdi			Mixed Taxa		
Sediment Parameter	R ²	b ₁	b2	R ²	b ₁	b2	R ²	b ₁	b ₂	
Aldrin	0,243	0.224	0,075	0,592*	0.542*	0.130	0.256*	0.231*	0.095	
a-BHC	0.628*	0.501*	0.175	0.478*	0,432*	0.117	0.425*	0,423*	900.0	
B-BHC	0,633*	0.778*	-0.283	0.374	0,358*	0,049	0,281*	0.288*	-0.036	
7-BHC	0.230	0,121	0.184	0,222	0,176	960.0	0,161	0.058	0.146	
a-chlordane	0,714*	0.572*	0,192	0.539*	0,367*	0,301*	*605.0	0,502*	0.023	
γ -chlordane	0.711*	0,763*	-0.082	0,360	0,345*	0,043	0.514*	0.526*	-0.061	
Dieldrin	0,622*	*0*9*0	-0.028	0.571*	0.522*	0.126	0,315*	0,308*	0.020	
DMDT	0.394	0.162	0,269	0,615*	0,555*	0.151	0.189	0,192	-0,010	
Endosulphan 1	0,468	0.517*	860.0-	0,455*	0,423*	0.087	0.275*	0.274*	0.004	
Endosulphan II	0.467	0,411	0.082	0.572*	0.524*	0,127	0,336*	0,341*	-0.022	
Endrin	0.290	-0.118	0,361	0.570*	0,523*	0,125	0,147	0,123	0,060	
Endosulphan sulphate	0.340	0.179	0.272	0.622*	0.566*	0,142	0,331*	0.157	0,279*	
Heptachlor epoxide	0.501	0.677*	-0,300	0.555*	*605.0	0,119	0.222	0,246	-0.052	
Heptachlor	0.818*	0.939*	-0.213	0,291	0,280	0.034	0,329*	0.336*	-0.029	
Mirex	0.821*	0.913	-0.156	0.274	0.256	0.050	0,362*	0,361*	0.001	
Oxy-chlordane	0.690	2.45	-1.85	0.541*	*464.0	0.115	0,315*	0,315*	00000	
PCB	0,772*	0.784*	-0.016	0.414*	0.478*	-0.184	0.583*	0.595*	-0.076	
DDD-d'd	*00.70	0.220	0.526*	0.574*	0.435*	0,270	0.427*	0.431*	-0.018	
p,p-DDE	0.332	0.117	0,221	0.683*	0,701*	-0.029	0.374*	0,386*	-0.031	
P.P-DDT	0,658	0.023	0,638	0.508*	* 464.0	0.044	0,251	0.253*	900.0-	
HCB	0,334	-0.359	0.662	0.602*	0.378	0.266	0.508*	0,085	0.429	

* Indicates statistical significance (p < 0.05) of model (R²) based on F-test or standard partial regression coefficient (b) based on t-test.

Model I:
$$\frac{C}{\text{lipid}} = \frac{b_1}{\text{TOC}} + \frac{c_s}{\text{TOC}}$$

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See text page 3.6 for definition of model terms. TOC was not significantly correlated with SE.

Differences between isomers (e.g., α -, β -, γ -BHC) in the level of significance of the model are probably due to differences in the amount of data above detection limits. For some isomers, there are very little data above detection. Additional data from highly contaminated areas, and/or improvements in analytical techniques, will increase the usefulness of the database.

The results suggest, in general, that the McFarland-Rubinstein model will be useful in prediction of bioaccumulation potential. However, the amount of quantitative data (above detection limits) must be considered as part of the model verification process. In a data set with numerous observations 'less than detection' in both tissue and corresponding sediment samples, any relationship between lipid content of tissue and TOC in sediments can produce a spurious relationship between lipid and TOC-normalized contaminant concentrations. Lipid and TOC were not related (p > 0.01) in the MOE In-Place Pollutants Program data.

3.2 Community Structure-Sediment Quality Relationships

Total organism density and species diversity are often used as indicators of benthic community health status, and these indicators have been related to various community stress factors, including sediment pollution. Krieger (1984) and Fitchko (1986a) have reviewed such community structural responses. As a general rule, density increases and diversity is reduced as pollution-tolerant taxa replace less tolerant forms. However, density decreases again as toxic thresholds of the tolerant taxa are approached. In addition, habitat factors can influence both density and diversity, confounding relationships between these community indicators and pollution levels.

The MOE In-Place Pollutants Program data set includes density and Shannon-Wiener diversity (H') measures since 1985. These were examined, as part of the present study, for relationships to heavy metal and organic contaminant concentrations in sediments. More sophisticated measures of community structure, based on cluster and discriminant analysis of species densities, are possible using the MOE In-Place Pollutants Program data. These methods are discussed in Section 2.4, but the actual analysis goes beyond the scope of this study.

3.2.1 Heavy Metal Relationships

Table 3.4 shows the density and diversity correlations with heavy metals in bulk sediments. Chemical analysis of sediments was restricted to the fine particulate fraction (<63 u). Most of the significant (p<0.01) density correlations were positive (r=0.32 to 0.55 for manganese, nickel, chromium, arsenic and cadmium in ascending order of magnitude). Lead was negatively correlated with density (r=-0.36). Diversity was poorly correlated with bulk sediment concentrations, the only significant correlation involving zinc (r=0.31).

Correlations of density and diversity with metal concentrations in particular sediment fractions have not been determined. The correlations based on bulk sediments do not suggest a definite pollution response since diversity is not reduced in association with metals. Possibly both densities and metals are associated with habitat characteristics such as sediment particle size.

3.2.2 Organic Contaminant Relationships

Table 3.5 shows the density and diversity correlations with organic sediment characteristics.

Density is more strongly correlated than diversity with pesticide and PCB contaminants. The most significant correlation coefficients, all exceeding r = 0.5, were for dieldrin, endrin, endosulphan sulphate and oxy-chlordane. The correlations were positive in all cases. These same parameters were most highly inter-correlated in the sediments, each with correlations to one of the other compounds in excess of r = 0.9 (Appendix 4, Table A4.3).

Diversity was weakly correlated with the same sediment contaminants. Negative correlation coefficients less than r = -0.20 were obtained for dieldrin, endrin, endosulphan sulphate and oxy-chlordane. A positive correlation of similar magnitude was obtained for HCB. Thus, a community response consistent with pollution impact is suggested for the first four pesticides mentioned above.

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TABLE 3.4: SIMPLE CORRELATIONS OF TOTAL ORGANISM DENSITY AND DIVERSITY WITH BULK SEDIMENT CONCENTRATIONS OF HEAVY METALS

Heavy		
Metal	Density	Diversity
Copper	0.1363	0.0357
Chromium	0.4333*	0.0427
Cadmium	0.5527*	-0.1597
Iron	0.3081	-0.0976
Lead	-0.3605*	0,2911
Zinc	-0.0556	0.3146*
Arsenic	0.5133*	-0.0326
Manganese	0.3249*	-0.3140
Nickel	0.4148*	-0.0696

^{*} Indicates statistical (not biological) significance of correlation coefficient (p < 0.01).

TABLE 3.5: CORRELATION OF TOTAL ORGANISM DENSITY AND SHANNON-WEINER DIVERSITY WITH ORGANIC CONTAMINANTS IN SEDIMENTS

Sediment	Correlation	Coefficient for:
Parameter	Density	Diversity
Aldrin	-	-
α-BHC	-0,057	0.126
β-BHC	-	-
γ-BHC	-	-
α-chlordane	-0.026	-0.096
γ-chlordane	-0.064	-0.153
Dieldrin	0.581*	-0.220
DMDT	-0.015	-0.046
Endosulphan I	0.098	0.169
Endosulphan II	-0.048	0.004
Endrin	0.523*	-0.209
Endosulphan sulphate	0.507*	-0.221
Heptachlor epoxide	0,299*	0.017
Hep tachlor	~	-
Mirex	-	0.050
Oxy-chlordane	0.508*	-0.220
PCB	-0.079	-0.178
p,p-DDD	-0.061	-0.007
p,p-DDE	-0.192	-0.055
p,p-DDT	-	-
НСВ	-0.086	0.287*

Indicates no coefficient computed due to lack of variation in bulk sediment concentrations.

^{*} Indicates statistical (not biological) significance of correlation coefficient (p < 0.01).

3.3 Workplan B Summary

Attempts to predict body burdens of persistent toxic chemicals in aquatic organisms, based on chemical characteristics of sediments, have followed different approaches for metals and organic compounds. For metals, tissue concentrations have been related to concentrations of contaminants in particular chemical fractions identified as source fractions for contaminant uptake by benthic biota. For organics, tissue concentrations have been related to bulk sediment concentrations of contaminants, taking into account modifying properties of both sediments and biota (e.g., total organic carbon, lipid content). These two approaches were tested, in the present study, using metal, pesticide and PCB data from the MOE In-Place Pollutants Program.

Heavy metal determinations, as part of the MOE In-Place Pollutants Program, have included arsenic, cadmium, chromium, copper, iron, lead, manganese, nickel and zinc in biota (primarily oligochaetes and sculpins) and in six fractions of the fine particulate component (< 63 u) of sediments (interstitial water, IW; cation exchangeable, F1; easily reducible, F2; organic complex, F3; Fe/Mn hydroxide, F4; and residual). Simple correlations between dry weight, gut corrected tissue concentrations and dry weight concentrations in fractions and bulk sediments were computed for oligochaetes, sculpins and a pooled data set (all taxa). In addition, correlations between bottom water concentrations (1 m above the bottom) and concentrations in fractions and bulk sediments were determined.

Good correlations between bottom water and interstitial water were obtained for arsenic, copper, manganese and nickel. In addition, iron was positively correlated with F2 and F4, manganese with most fractions and with bulk sediments, and nickel with F2.

Tissues were less well correlated with sediment fractions, and differences between taxa were suggested. Based on these correlations, it appears that significant prediction of tissue concentrations may be possible for some metals (arsenic, cadmium, copper, iron and nickel in oligochaetes; arsenic, iron, lead and manganese in sculpins). Results were not promising for chromium or zinc.

More complex relationships to ratios or sums of several sediment fractions have not been investigated. Possibly, predictive power could be increased by use of more complex

predictive functions; however, interpretation of underlying uptake mechanisms would be more difficult.

Organic determinations, as part of the MOE In-Place Pollutants Program, have included aldrin, BHC (α , β , γ), chlordane (α , γ), dieldrin, DMDT, endosulphan (I, II), endrin, endosulphan sulphate, heptachlor epoxide, heptachlor, mirex, oxy-chlordane, PCB, p,p-DDD, p,p-DDE, p,p-DDT and HCB in biota and bulk sediments. Several modified McFarland-Rubinstein regression models were tested for prediction of lipid-normalized contaminant concentrations in tissues from total organic carbon-normalized concentrations in sediments, solvent extractible-normalized concentrations in sediments, and percent fine material in sediments (silt + clay).

In general, the results indicate that a simple McFarland-Rubinstein model, based entirely on total organic carbon-normalized concentrations in sediments, will perform as well as the more complex models tested. Differences in contaminant behaviour between taxa were suggested. Behaviour of α -BHC, α -chlordane, heptachlor and mirex fit the model for oligochaetes but not sculpins, while aldrin, DMDT, endosulphan I and II, endrin, endosulphan sulphate, heptachlor epoxide, oxy-chlordane, p,p-DDE, p,p-DDT and HCB fit the model for sculpins but not oligochaetes. Five compounds (α -BHC, α -chlordane, dieldrin, PCB and p,p-DDD) fit the model for both oligochaetes and sculpins.

Total organism density and benthic community diversity were correlated with concentrations of dieldrin, endrin, endosulphan sulphate, oxy-chlordane and PCB. Density correlations were positive and diversity correlations were negative, suggesting a community response to organic contaminants. Similar community responses were not obtained for heavy metals.

4.0 WORKPLAN C - STRATEGIES DEVELOPMENT

4.1 Background

The objective of Workplan C is to outline strategies for developing numerical sediment quality objectives for Ontario. These strategies will be designed to address:

- biological considerations (acute and chronic toxicity, bioconcentration, bioaccumulation/biomagnification, benthic community structure, fish flesh tainting, etc.);
- o occurrence of pathological conditions, such as lesions, tumours and deformities in aquatic organisms; and
- o water quality degradation due to contaminant release from the sediments.

As discussed previously, protocols for sediment quality evaluation have evolved over the previous ten to 15 years in North America, primarily in response to concerns over toxic substances in dredge spoils. For example, the U.S. EPA/U.S. COE (1977) developed guidelines for the bioassessment of proposed dredging and disposal projects in the marine environment, aimed primarily at continuous dredge spoil disposal operations. BEAK has previously reviewed these and other more recent protocols to further the development of sediment assessment protocols for Ontario and the Great Lakes (BEAK, 1980; Craig, 1984; Munawar et al., 1984; BEAK/OCEANCHEM, 1986). Current strategies for evaluation of the potential for water quality degradation due to sediment contamination include bulk chemical analysis, the relatively simple U.S. EPA elutriate test, as well as sequential extraction procedures (e.g., Tessier et al., 1984). However, simple examination of the chemistry of sediments and extracts provides little information on the potential effects on biota (e.g., Hoke and Prater, 1980), indicating the need for protocols based on bioassessment.

The Dredging Subcommittee (1982) supports a site-specific approach to dredging project evaluation, based on both sediment chemistry and on some form of bioassessment, but concluded in 1982 that standard methodologies and interpretive criteria for sediment bioassessment were yet unavailable. Subsequently, the Dredging Subcommittee (1986) concluded that routine procedures for determination of acute toxicity of sediments had been established, although the Committee also concluded that further development of

evaluation procedures for assessment of chronic effects and bioaccumulation were required.

The Criteria and Standards Division of the U.S. EPA has recently initiated a program to develop sediment quality criteria. These sediment quality criteria are to be used in conjunction with water quality criteria to protect U.S. freshwater and saltwater environments and their uses, including fisheries, recreation and drinking water. Section 304(a) of the Clean Water Act authorizes the U.S. EPA to develop and implement sediment criteria analogous to the U.S. EPA water quality criteria. This initiative recognized that, while ambient water quality criteria are an important component in assuring the health and uses of an aquatic environment, contaminated sediments may be responsible for significant adverse effects on certain aquatic organisms, as well as designated water use, even when ambient water quality is in compliance with water quality criteria.

Long and Chapman (1985) proposed a "sediment quality triad" as an approach or concept applicable to development of a sediment quality index. The triad consists of three categories of measurements:

- 1. concentrations of toxic chemicals,
- 2. toxicity of environmental samples, and
- 3. evidence of modified resident biota, preferably infauna.

It was argued that measurement of contaminant concentrations alone provide no indication of biological impact, but are needed to determine the degree and nature of contamination. Bioassay testing of sediments can establish the toxicological significance of the contaminants. However, since bioassays are usually performed in a laboratory environment, they may not accurately reflect the conditions under which resident biota may be exposed to the toxic contaminants. Measures of changes in resident biota exposed to or living in the sediments are required to corroborate the laboratory bioassay data. Data on changes in the benthic macroinvertebrate community structure alone, however, may provide misleading evidence of in situ toxic contaminant effects, since benthic communities may be overwhelmingly modified by recruitment cycles, predation, competition, natural events, and subtle non-pollution related variations in the physicochemical properties of the sediments or overlying water.

Subsequently, Chapman (1986) used the sediment quality triad approach to derive quantitative sediment quality criteria for specific contaminants. The data sets used were obtained from studies of Puget Sound. The data were analyzed by linear correlation, factor and hierarchical cluster analysis to determine groupings showing strong covariance in their sediment concentrations. Three dominant and representative contaminant groups were distinguished in the analysis and were selected for further study: high molecular weight combustion polyaromatic hydrocarbons (CPAHs), total PCBs and lead. The concentration data for these three groups were quantified as mean values for each embayment area within Puget Sound. Three types of sediment bioassay data were considered: the amphipod Rhepoxynius abronius ten-day acute lethality test; the oligochaete Monopylephorus cuticulatus 8-hour respiration effects test; and the 72hour fish cell anaphase aberration test. The sediments tested were considered to be toxic, or not, based on determination of significant (p = 0.05) differences from controls. Bioassay responses were quantified as the percentage of total tests that were toxic, by embayment. In addition, available data on the frequency of occurrence of liver lesions in English sole were reviewed and frequency values were summed for each embayment.

The data for sediment contaminant concentrations, sediment bioassay and bottom fish histopathology indicated that biological effects increased with a corresponding increase in concentrations of sediment contaminants. The macro-scale data comparisons delineated contaminant concentration values below which biological effects were low or minimal and above which biological effects were always high, as well as intermediate contaminant concentrations representing an area of uncertainty between the high and low concentrations (Table 4.1). Derivation of these concentration values ignores which particular contaminants may be causing the observed biological effects, and provides a conservative estimate based on interactions (e.g., synergism or antagonism) between complex contaminant mixtures that may individually or in combination be responsible for the observed effects.

The concentration values determined by the triad approach were compared to sediment quality criteria values derived theoretically by the partition coefficient approach by two other studies (Table 4.1). The ranges of criteria derived in those studies are based osediments with a 2% organic carbon content. Comparing these predicted values with those obtained from field data, the predicted lead and PCB values fell within the "area of uncertainty", whereas the CPAH values fell below the range at which no or minimal

	Criter	ia Concentration	(ug/g)
Criteria Description	Lead	CPAHs	Total PCBs
No or minimal biological effects	≤50	≤3,8	≤0.1
Major biological effects	≥130	≥6,8	≥0.8
Area of uncertainty	>50<130	> 3,8 < 6,8	> 0.1 < 0.8
Partition coefficient theoretical calculations	60-66	0.07-2.24 ²	0.10-0.48 ³

¹ After Chapman (1986).

² Naphthalene, chlorinated naphthalene and fluoranthene.

³ Aroclor 1254.

biological effects were demonstrated. Chapman (1986) concluded that the sediment quality criteria values based on sediment toxicological data provide a quantitative estimate that is in the range of, but which may be more realistic than, theoretical calculations.

The U.S. EPA adopted a phased approach to developing sediment quality criteria. In the first phase, the U.S. EPA sponsored two Sediment Quality Criteria Workshops. At the workshops, experts on sediment chemistry and toxicology identified and described several approaches or strategies for deriving sediment quality criteria for three classes of chemical contaminants: nonpolar organics, heavy metals and polar organics. The U.S. EPA currently is supporting several research projects to evaluate and refine some of the methods proposed at the workshop for developing sediment quality criteria. It is anticipated that results from these studies will lead to the selection of an optimum methodology for the development of sediment quality criteria. A description of a few of these projects, based on reports made available to BEAK, is provided below.

For their compilation of a national inventory of sediment contaminant concentrations, Bolton et al. (1983) used threshold concentrations to assess differences in the levels of various chemicals in sediments (Table 4.2). The threshold concentration values were calculated using the sediment-water equilibrium partitioning approach (JRB, 1984) and/or were derived from Paylou and Weston (1984).

In this equilibrium partitioning approach, the assumption is made that the distribution of a contaminant between the sediment phase and the soluble phase of interstitial water in equilibrium with the solid phase is described by the sediment-water partition coefficient of the contaminant. Based on literature review, Pavlou and Weston (1984) found that sediment organic carbon content was the primary environmental factor influencing partitioning and, therefore, recommended that partition coefficients be normalized to organic content. A preliminary predictive equation was developed that related organic carbon-normalized sediment-water partition coefficients ($K_{\rm oc}$) to octanol-water partition coefficients ($K_{\rm oc}$). If the water quality criterion value is taken to be the maximum acceptable concentration of the contaminant in solution in interstitial water, then the threshold (or permissible) concentration of the contaminant in the bulk sediment is calculated, based on the sediment organic carbon-normalized $K_{\rm cc}$ for the contaminant.

TABLE 4.2: THRESHOLD CONTAMINANT CONCENTRATIONS 1

Concentration² (ug/g dry weight bulk sediment) Contaminant Arsenic 33 31 Cadmium Copper 136 132 Lead Mercury³ 0.8 760 7inc Aldrin 0.021 γ-BHC 0.012 13 DDD DDE 28 DDT 0.006

After Bolton et al. (1985).

The concentration values were adjusted to a whole sediment basis on the assumption that an average sediment contains 4% total organic carbon (TOC). The 4% value for average TOC is high for many freshwater sediments, with a more typical value likely in the 1 to 2% range. If 2% TOC had been used for the calculation of TOC-normalized sediment threshold concentrations for contaminants, the values would be one-half those listed in this table.

³ The value of 0.8 ug/g was not corrected for organic carbon. Correction for organic carbon would have resulted in a mercury concentration of 0.03, which is considerably lower than the concentration of mercury found in most natural sediments.

The advantages and disadvantages of this approach were delineated by Bolton et al. (1985) to permit preliminary evaluation regarding relevancy to biological thresholds. Advantages of the sediment-water equilibrium partitioning approach include:

- o sediment quality criteria can be readily developed for those contaminants with water quality criteria, as well as those which are assigned water quality criteria in the future; in this case, the large toxicological database incorporated in the water quality criteria forms the technical basis for the development of sediment quality criteria; and
- preliminary values for sediment quality criteria for specific contaminants are available that can then be verified by future field and laboratory studies.

Disadvantages of this approach include:

- sediment quality criteria cannot be established for those compounds without water quality criteria;
- there is no accounting for any potential increase in contaminant body burden due to ingestion of or direct contact with contaminated sediments above that obtainable strictly by absorption from surrounding waters;
- the assumption of contaminant equilibrium between sediment and interstitial water, inherent in this approach, may not always hold in natural systems;
- o sediment quality criteria developed for metals have a very high associated uncertainty, since the sediment organic carbon-water partition coefficient values calculated for the same metal by different investigators and/or under different physicochemical regimes may differ by several orders of magnitude; and
- o the approach does not take into account the modifying effects of soluble and particulate organic matter in interstitial water on partitioning and bioavailability of nonpolar organic contaminants.

Kadeg et al. (1986) further reviewed the available literature on partitioning of nonpolar organic contaminants, refined the empirical $K_{\rm oc}/K_{\rm ow}$ equations developed by Pavlou and Weston (1984) and calculated "permissible sediment contaminant concentration" values

using the updated $K_{\rm oc}/K_{\rm ow}$ relationships (Table 4.3). Variation of reported $K_{\rm oc}$ values for specific contaminants was quite high, and was attributed to such factors as sorbent concentration effects (Voice and Weber, 1983), particle effects (DiToro and Horzempa, 1982), variation in the physicochemical regime, and/or differing laboratory techniques. In many instances, the variability in $K_{\rm ow}$ for a specific contaminant was also large, due in part to the lack of standardized methodologies for determining $K_{\rm ow}$, as well as physical and chemical factors, e.g., particle effects, dissolved organic matter.

The following regression equation, significant at the 0.0011 level, was determined for pesticides:

$$\log K_{OC} = 0.717 \log K_{OW} + 0.802$$

A strong correlation (r = 0.869) was found between $K_{\rm oc}$ and $K_{\rm ow}$ values. Therefore, $K_{\rm ow}$ values could be used to predict $K_{\rm oc}$ values in the absence of empirical data. The resulting regression agreed well with that developed by Kenaga and Goring (1980). Kadeg et al. (1986) recommended probabilistic uncertainty analysis on the empirical equations and the development of laboratory and field programs to verify and further refine the predictive equations.

Neff et al. (1986) empirically evaluated the Screening Level Concentration (SLC) approach for nonpolar organic contaminants in sediments, and assessed its strengths and weaknesses for use in conjunction with other methods for deriving sediment quality criteria. The SLC approach uses field data on the co-occurrence in sediments of benthic infaunal invertebrates and different concentrations of a specific nonpolar organic contaminant. The SLC is an estimate of the highest concentration of a particular nonpolar organic contaminant in sediment that can be tolerated by approximately 95% of benthic infauna.

SLCs are calculated from organic carbon-normalized contaminant concentrations rather than concentrations in bulk sediment. As discussed previously, this normalization is based on the premise that bioavailability of nonpolar organic contaminants from sediments is dependent upon the organic carbon content of the sediment, the lipid content of the organism, and the relative affinities of the chemical for sediment organic carbon versus organism lipid (Kadeg et al., 1986). A nonpolar organic contaminant will

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PERMISSIBLE SEDIMENT CONTAMINANT CONCENTRATIONS (PSCC)¹ FOR PESTICIDES TABLE 4.3:

	Water	Water Quality Criterion (ug/L)			PSCC (ug/g organic carbon)	SC iic carbon)	Acute Threshold Concentration ² (Paylor and Weston, 1984)
Contaminant	Acute	Chronic	Log Kow	K _{oc} (x10 ⁵)	Acute	Chronic	(ug/g organic carbon)
Aldrin	1.3	,	6.12	1.55	201	1	0,52
γ -BHC	0.083	,	4.00	0.047	0.374	,	r
Chlordane	60.0	0.004	3.86	0.037	0.334	0.0148	
DDD	1.83	1	5.56	0.614	111	1	325
DDE	73	,	5.60	0.656	094	,	700
DDT	0.13	1	6.07	1.42	18.5	•	21
Dieldrin	2,5	0,0019	4.95	0,224	56	0.0426	•
Endrin	0.037	0.0023	44.44	0.097	0.358	0.0222	
Heptachlor	0,053	0,0036	45.4	0,114	0,604	0,0411	

¹ After Kadeg et al. (1986), based on regression equation for pesticides (see text).

² As reported in Pavlou and Weston (1984), based on single "universal" equation for organic contaminants (see Table 4.1).

³ One-half the lowest concentration at which toxic effects have been noted, as reported in U.S. EPA (1980p); actual water quality criterion value, when established, is likely to be different.

be distributed among the three phases (i.e., the sediment organic fraction, the tissue organic fraction and the interstitial water), in proportion to the respective sediment organic carbon-water and tissue lipid-water partition coefficients of the contaminant. Therefore, the bioavailability and, by inference, the toxicity of a nonpolar organic contaminant in sediment will be proportional to the ratio of the partition coefficient of the contaminant in the tissue lipid fraction to the partition coefficient of the contaminant in the sediment organic fraction, and the sediment organic carbon concentration.

To calculate an SLC, large databases are required that contain synoptic data on the concentrations of the specific nonpolar organic chemicals, as well as total organic carbon in the sediments and the species composition of the benthic infauna. A cumulative frequency distribution of all stations (samples) at which a particular species is present is plotted against the organic carbon-normalized concentration of the specific contaminant in sediment. The concentration of the contaminant at the locus representing the 90th percentile of the total number of samples (stations) at which the species was present is estimated by interpolation, and termed the species screening level concentration (SSLC). Subsequently, the SSLCs for a large number of species are plotted as a frequency distribution. The concentration above which 95% of the SSLCs are found is termed the SLC (see Appendix 5).

Based on sufficient available data, SLCs were calculated in this way for five contaminants in freshwater sediments (chlordane, DDT, dieldrin, heptachlor epoxide, total PCBs). For these contaminants, the benthic macroinvertebrate taxa most frequently in the samples were Oligochaeta and Ephemeroptera. A summary of the SLC results for the five contaminants is presented in Table 4.4.

The range and distribution of contaminant concentrations in the database have a marked effect on the calculated value of the SSLCs and, therefore, the SLCs generated. For example, the SLC for PCBs in freshwater sediments was 15 times lower than the corresponding value for saltwater sediments. Moreover, there was a 225-fold difference in the SLCs for DDT in freshwater and saltwater sediments. The concentration of contaminants in freshwater sediments tended to be low (as evidenced by the many zero contaminant values), whereas the saltwater database tended toward more highly contaminated sediments. Based on these observations, it was concluded that the

SUMMARY OF SCREENING LEVEL CONCENTRATION RESULTS $^{\rm I}$ TABLE 4.4:

Contaminant	Contaminant Conc. Range (ug/g dry sed.)	Organic Carbon Normalized Conc. Range (ug/g org. carbon)	No. of Taxa Included in SSLC Analysis	SSLC Range (ug/g org. carbon)	Calculated SSLC (ug/g org. carbon)
Chlordane	0.0-1.0	0.0-25.1	16	0.124-8.5	860.0
DDT	0.0-30.7	0.0-3,520	21	0.189-20.0	0.190
Dieldrin	0.0-1.0	0.0-24.5	16	0,026-1,0	0.021
Heptachlor expoxide	0.0-1.0	0.0-29.1	12	0,013-4,9	0.008
PCBs	0,0-23,13	0.09-0.0	21	0.286-103.4	0.230

1 After Neff et al. (1986).

freshwater SLC values may be conservative and the saltwater SLC values may be too high.

The SLC calculation process, by its very nature, makes no a <u>priori</u> assumptions about a causal relationship between a given contaminant concentration in sediments and the presence or absence of a particular species of benthic infauna. For example, it is possible to have a data set in which all concentrations of a specific contaminant are well below the concentration in sediments that would adversely affect the distribution of benthic infauna. SLCs calculated with such a data set would be conservative, and the SLC would have little regulatory relevance. On the other hand, if most data are from heavily contaminated areas, most of the pollution-sensitive species would be absent, and the SLC would be based primarily on pollution-tolerant species. In this case, the SLC would be too high. As the range of contaminant concentrations upon which the SLC is based increases, the likelihood of these types of biases in the SLC decreases.

Neff et al. (1986) concluded that the SLC approach had demonstrated sufficient merit to warrant further evaluation and elaboration. Given a large enough database and minor modifications to the methods for calculating SSLCs and SLCs, the approach should provide a conservative estimate of the highest organic carbon-normalized concentrations of specific contaminants in sediments that can be tolerated by approximately 95% of the benthic fauna. It is essential that the database contain organic carbon-normalized concentrations of specific contaminants in sediment that span a wide range, and include values from locations known to be heavily contaminated and to have impacted benthic macroinvertebrate communities. Low and intermediate sediment contaminant concentrations are also required to ensure that sensitive species are included in the analysis. It was cautioned that, before SLCs could be used in a regulatory context, the databases upon which they are based must be subjected to a rigorous quality assurance review, with both the biological and chemical data evaluated for accuracy, comparability and representativeness.

Most recently, Poston and Prohammer (1986) proposed a laboratory evaluation of a protocol for sediment toxicity testing of nonpolar organic compounds. The protocol is based on the carbon normalization theory, discussed previously, which states that toxicity of nonpolar organic compounds to benthic infaunal organisms is dependent on the total organic content of the sediment. The fundamental assumptions underlying this protocol development are:

- toxicity of the nonpolar organic compounds is generally attributed to the compound found in interstitial water, not adsorbed to the sediments:
- sediments with high total organic carbon have a greater capacity to adsorb nonpolar organic compounds; and
- o the relationship between the concentration of nonpolar organic compounds in sediments and interstitial water is defined by the aqueous solubility of nonpolar organic compound, the octanol water partition coefficient (K_{ow}), and the concentration of sediment total organic content (Staples et al., 1985).

Therefore, as sediment total organic carbon levels increase, the toxicity expressed per gram of sediment decreases. This relationship can then be normalized by expressing the toxicity of the nonpolar organic compound in terms of the total organic carbon concentration in the sediment.

Three nonpolar organic compounds, γ -BHC, DDT and endrin, were suitable for testing based on the following criteria, to maximize the potential for evaluating the influence of sediment total organic carbon on toxicity:

- o the reported median lethal concentration, or median effective concentration (LC50 or EC50, respectively), for 48- or 96-hour acute toxicity tests with the test organism (amphipods) must be at or below 20% of the reported solubility of the toxicant in water;
- o the sediment sorption coefficient (K_{OC}) should be greater than 1,000 to ensure that the toxicant will establish reasonable concentrations in interstitial water to elicit a toxic response in the test organisms; and
- o the toxicant must have a low vapour pressure, i.e., less than 0.001 mm mercury, to ensure that excessive volatilization does not cause a loss of toxicant when amending the sediment.

The general approach involves a screening water column test to establish the toxicity of the toxicants in the water, a screening sediment toxicity test with three levels of sediment total organic carbon, to establish the range of sediment toxicant concentrations to be used in a definitive test, and the definitive sediment toxicity test to provide tenday LC50 values for the toxicants at three levels of sediment total organic content.

Subsequently, the relationship between sediment total organic carbon and toxicity will be used to evaluate the organic carbon normalization theory.

4.2 Approaches to Sediment Quality Criteria Development

The development of scientifically sound sediment quality criteria that can be applied widely to sediments from different sources is a difficult undertaking. Contaminants interact in complex, often poorly understood ways with sediment particles, and may be present in sediments in a variety of sorbed or solid forms. As discussed in Workplan A, contaminants associated with sediments are much less bioavailable and toxic to benthic biota than when in solution in the water. At the same time, contamination of bottom sediments by metals and persistent chlorinated organics provides a long-term source of these contaminants to the overlying waters and aquatic organisms, even after major reductions in or cessation of contaminant inputs (e.g., Young et al., 1977; Larsson, 1985). Unfortunately, there is no known simple relationship between the concentration of a contaminant in sediment and its toxicity to benthic fauna in contact with that sediment.

The approaches to sediment quality criteria development, which are under consideration by regulatory agencies or otherwise appear promising, have been recently described and summarized by Bolton et al. (1985) and Tetra Tech (1986). These approaches include:

- background approach,
- water quality criteria approach,
- sediment-water equilibrium partitioning approach,
- o sediment-biota equilibrium partitioning approach,
- o field bioassay approach,
- o screening level concentration approach,
- o apparent effects threshold approach, and
- spiked bioassay approach.

A short description of each of these approaches follows. Examples and calculations are detailed in Appendix 5.

4.2.1 The Background Approach

In the background approach, sediment contaminant concentrations at a particular location are compared to concentrations from reference (background) sites, where contaminant levels are deemed to be acceptable. Mudroch et al. (1986) provide an example of this approach. They have undertaken an evaluation of the existing MOE guidelines for dredged material open water disposal based on a comprehensive review of the background and surficial concentrations of contaminants in sediments, including harbours, river mouths, bluffs and embayments of the Great Lakes.

The primary advantage of the background approach is that it has minimal data requirements. The establishment of background contaminant concentrations does not require the collection of extensive field data, particularly in areas, such as the Great Lakes, where historical data are available. This approach is the only method for establishing sediment quality criteria values that does not require quantitative toxicological data for the specific contaminants in sediment.

The limitations of this approach are the difficulties inherent in developing a technically and legally defensible method of selecting a "suitable" reference area, or determining what is an "acceptable" level of contamination.

4.2.2 The Water Quality Criteria Approach

In the water quality criteria approach, the concentrations of specific contaminants in interstitial waters are measured directly and compared with existing water quality criteria. If contaminants in sediments are also measured, the relationship of sediment to interstitial water concentrations can be used to derive sediment quality criteria from the water quality criteria.

The principal advantage of this approach is that it relies on existing toxicological databases established for water quality criteria development, and only requires site-specific collection of chemical data. For contaminants lacking water quality criteria, the toxicity data for waterborne contaminants in Appendix 2 provide the basis for development of such criteria.

A critical limitation of this approach is obviously the availability of water quality criteria for specific contaminants. Another major limitation of this approach is that toxicological data used to establish the water quality criteria were derived from sediment-free bioassays primarily with nektonic organisms. These data do not take into account the modifying (mainly ameliorative) effects of soluble and particulate organic matter in interstitial water on bioavailability and toxicity of specific contaminants. On the other hand, the potential increase in contaminant body burden due to ingestion of or direct contact with sediment above that obtainable strictly by absorption from surrounding waters are also not accounted for in the development of water quality criteria. An additional limitation is that methods for obtaining and analyzing representative interstitial water are still being developed.

4.2.3 The Sediment-Water Equilibrium Partitioning Approach

The sediment-water equilibrium partitioning approach has been undertaken by Pavlou and Weston (1984), Bolton et al. (1985) and Kadeg et al. (1986), as discussed in Section 4.1 (see Tables 4.2 and 4.3). This approach is based on the assumption that the distribution of contaminants among different compartments in the sediment is controlled by a continuous equilibrium exchange among sediment, organism, interstitial water and overlying water. Using this approach, contaminant-specific partition coefficients are determined (generally expressed in terms of organic carbon content in the sediment) and used to predict the distribution of the contaminant between sediment and interstitial water. Subsequently, the predicted contaminant concentration in the interstitial water is compared with established water quality criteria. Alternatively, a sediment quality criterion concentration value (normalized for organic carbon content) for a specific contaminant can be calculated based on an interstitial water concentration equivalent to the water quality criterion value for the contaminant. Details of the computations undertaken in this approach are provided in Appendix 5.

The sediment-water equilibrium partitioning approach uses the same toxicological database as the water quality criteria approach, but avoids the difficulties associated with the direct measurement of contaminant concentrations in interstitial water. For contaminants lacking water quality criteria, toxic effects of waterborne contaminants (Appendix 2) provide the basis for development of such criteria.

The predictive relationships involving K_{OW} and K_{OC} for nonpolar organic compounds which forms the basis of this approach cannot be reliably determined for ionizable organic pollutants and trace metals, which can be strongly influenced by physicochemical factors other than organic carbon content. These uncertainties related to the effects of variations in the site-specific physicochemical regime on metal and organic contaminant distributions among phases complicate quantification of these contaminant distributions for use in defensible sediment quality criteria. Other limitations include the uncertainty of the equilibrium assumption for all aquatic environments, variations in reported K_{OW} values, and the representativeness of laboratory determinations of K_{OC} values based on water column-suspended solids systems rather than in situ sediment-water systems. Furthermore, limitations in the use of water quality criteria to evaluate contaminant concentrations in interstitial waters have been discussed in the description of the previous approach.

It is possible to overcome this last limitation by using interstitial water/overlying water distribution coefficients, or more sophisticated models of diffusion from the interstitial compartment (e.g., BEAK, 1987c). Thus, sediment quality criteria would be derived to produce contaminant concentrations in compliance with water quality criteria in the water column above the sediment.

4.2.4 The Sediment-Biota Equilibrium Partitioning Approach

The sediment-biota equilibrium partitioning approach is also based on the assumption that the distribution of contaminants among different compartments in the sediment is controlled by a continuous equilibrium exchange among sediment, organism, interstitial and overlying waters. Using this approach, contaminant-specific partition coefficients are determined and used to predict the distribution of the contaminant between sediment and benthic organism and/or interstitial water and benthic organism. In this approach, it is assumed that hydrophobic pollutants associate predominantly with lipids in all aquatic organisms, and with organic carbon in all sediments, and that the affinity of lipids and organic matter in all organisms and sediments, respectively, is the same. It is also assumed that the equilibrium distribution of nonpolar organic contaminants between lipids and sediment organic carbon (i.e., the bioconcentration factor) is constant regardless of the type of organism or sediment, and regardless of the specific compound. This assumption is not necessary if organism-specific bioconcentration

factors are established for specific compounds in laboratory or field studies. This partitioning approach establishes a sediment and/or interstitial water contaminant concentration below which benthic biota would be unable to attain a body burden of the contaminant in excess of a permissible limit. Tissue body burden limits can also be calculated on the basis of water quality criteria values. Computational details for the sediment-biota equilibrium partitioning approach are presented in Appendix 5.

The assumptions involved in this approach require extensive validation and study. Both sediment-biota and water-biota partitioning processes have to be quantified. Poor correlations between partition coefficients and bioconcentration factors have been observed with compounds that are rapidly metabolized by organisms. Furthermore, extensive body burden-effect data are required to establish permissible limits. Although limits have been established by the IJC, Health and Welfare Canada and the U.S. Food and Drug Administration for several contaminants in the edible tissues of commercial fish species, their applicability to environmental quality is not well founded, as they are designed for the protection of human health and take into account socioeconomic factors.

BEAK/OCEANCHEM (1986) has suggested the use of food chain biomagnification factors to work backward from acceptable body burdens in fish to acceptable body burdens in the benthos on which fish feed. This would seem to be an essential element to the sediment-biota partitioning approach, since acceptable benthic tissue concentrations have not otherwise been defined.

4.2.5 The Field Bioassay Approach

In the field bioassay approach, sediment quality criteria are established based on doseresponse relationships developed by exposing benthic organisms to field-collected sediments with known concentrations of contaminants and measuring mortality and sublethal effects and bioconcentration. These biological responses are compared quantitatively to effects observed in reference sediments. Sediment quality criteria values could then be established at contaminant concentrations that correlate with the statistically significant difference in mortality or other biological response between a test sediment and a control sediment.

Although this approach has the capacity to provide a holistic assessment of contaminant source availability and toxicological effects on benthic organisms, it cannot, in its simplest form, be used to establish specific sediment quality criteria values. The approach treats sediment toxicity as a measurement of the total effect of all toxic agents (even those that have not been identified and quantified). Therefore, this approach is useful for identifying sediments of environmental concern, but requires integration with other approaches to provide contaminant-specific sediment quality criteria values (e.g., see the Apparent Effects Threshold Approach).

4.2.6 Screening Level Concentration Approach

The screening level concentration (SLC) approach has been undertaken by Neff et al. (1986), as discussed in Section 4.1 (see Table 4.4). The SLC approach estimates the sediment concentration of a contaminant above which less than 95% of the total enumerated species of benthic infauna are present.

The use of field data on the co-occurrence of specific levels of sediment contamination and a resident benthic infauna has several intuitively appealing attributes. In this case, data on specific contaminant concentrations in sediments can be related to the presence or absence of species, species densities and/or species diversity. However, no a priori assumptions are made about a causal relationship between levels of sediment contamination and the distribution of benthic macroinvertebrate populations. Because no causal relationship is assumed, it is not necessary to take into account the wide variety of environmental factors, e.g., water depth, sediment type, etc., that influence benthic macroinvertebrate community structure. However, with actual observations from the field of the co-occurrence in the sediments of benthic macroinvertebrate populations and concentrations of specific contaminants, valid a posteriori inferences can be made about the range of contaminant concentrations in the sediment that the benthic infauna can tolerate.

Furthermore, contaminated sediments generally contain more than one contaminant at an elevated concentration. The benthic macroinvertebrate populations resident in the contaminated sediments are responding to the multiple contaminants present. Moreover, the populations that have been eliminated may have responded to the adverse effects of synergistic contaminant interactions. As a result, any sediment quality criteria value for

a specific contaminant derived by this approach will tend to be conservative. That is, assuming that synergistic interactions are operative, the derived contaminant concentration would be lower than the benthic infauna could tolerate if the specific contaminant alone was present in the sediment. Because of the infinite mix of contaminants possible and the natural heterogeneity of sediments, this conservative bias will tend to decrease as the database is increased.

The approach is not theoretically limited to any one kind of chemical contaminant, although organic carbon normalization, as recommended by Neff et al. (1986), limits its use to nonpolar organic compounds. With appropriate normalization, the approach could be applied to metals and ionizable organic compounds.

The SLC approach requires a considerable amount of field data that span a wide range of contaminant concentrations. It also requires that infaunal taxonomic identification be made at the species level. Furthermore, some a priori accounting for "natural" environmental factors may be required in assessing smaller benthological data sets. A final limitation concerning the influence of unmeasured contaminants, common to all the chemical-specific approaches, and especially empirical approaches that use field data to generate sediment quality criteria values, is discussed in the next subsection describing the apparent effects threshold approach.

4.2.7 Apparent Effects Threshold Approach

In the apparent effects threshold (AET) approach, the sediment concentration of a contaminant is identified above which statistically significant biological effects (e.g., mortality, benthic infauna population decreases) would always be expected. The AET concentrations are empirically derived from paired field data for sediment chemistry and a range of biological effects indicators. In this approach, two subsets of sediment samples are delineated. One subset includes those samples with a contaminant concentration below a maximum concentration for any sample at which there is no statistically significant biological effect. This subset can include samples that exhibited a statistically significant biological effect with contaminant concentrations below the maximum concentration. The second subset includes those samples with a contaminant concentration above a minimum concentration at which <u>all</u> samples are observed to have a statistically significant biological effect. This subset does not include samples that do

not exhibit a statistically significant biological effect. Therefore, the apparent effects threshold concentration is defined as the concentration above which <u>all</u> samples are observed to have a statistically significant biological effect.

AETs are not limited to site-specific biological indicators. They can also be established from biological effects data that are not site-specific, such as fish histopathology or fish bioaccumulation data. Biological indicators that are not site-specific will, however, introduce additional uncertainty to AET because they will require averaging of contaminant data over large areas.

The AET approach does not intrinsically require normalization; however, normalization of data to organic carbon content, metal hydroxide content or particle size may contribute to a refinement of sediment quality criteria values. For example, the comparison of samples with similar grain size distributions could minimize potential biological effects of natural environmental factors. Furthermore, there are no constraints on the type of contaminant (e.g., metal, nonpolar organics, ionizable organics) for which AETs can be established. By definition, observed biological effects always occur above the AET (for the given data set); hence, the approach provides a sediment contaminant concentration value that is based on non-contradictory evidence of environmental effects.

The AET approach requires the collection of extensive field data for contaminant concentrations and at least one biological response indicator. AET uncertainty due to interactive effects of contaminants should be decreased by the number of data sets that are used to generate AETs increase.

Another source of uncertainty common to all of the chemical-specific approaches is the possibility of effects being caused by unmeasured, covarying contaminants. If an unmeasured contaminant varies consistently in the aquatic environment with a measured contaminant, then the AET established for the measured contaminant will indirectly apply to or result in management of the unmeasured contaminant. In such cases, a measured contaminant would be used as an "indicator" for the unmeasured contaminant. If an unmeasured contaminant does not always covary with a measured contaminant, the effect should be discerned if a sufficiently large data set is used to establish an AET. Because AETs are set by the highest concentration of a specific contaminant in samples

without observed biological impacts, the AET will not be affected by less contaminated samples in which unmeasured contaminants cause biological effects.

If an unmeasured toxic contaminant does not covary with any of the measured contaminants, it is likely that neither the AET or any of the other contaminant-specific approaches reviewed could predict impacts at stations where the unmeasured contaminant is inducing toxic effects. However, predictive success can be tested in a validation of each contaminant-specific approach using field and/or laboratory experimental data.

4.2.8 Spiked Bioassay Approach

In this approach, dose-response relationships are determined by exposing test organisms to sediments that have been spiked with known amounts of contaminants. Sediment quality criteria values can then be determined using the sediment bioassay data in the manner that aqueous bioassays were used to establish water quality criteria.

In contrast to the field-based approaches described previously, the spiked bioassay approach can establish cause-and-effect relationships between contaminants and toxic biological responses. Contaminants can be tested individually or in combination. Furthermore, interactive effects of contaminant mixtures can be identified and quantified.

The major limitation of this approach is the amount of research effort required to test potentially toxic contaminants. The spiked bioassay approach has been used primarily for metals (e.g., Birge et al., 1977; Cairns et al., 1984; Francis et al., 1984; Nebeker et al., 1986a), although some preliminary bioassay work has been undertaken with sediments enriched with nonpolar organic contaminants (e.g., White, 1984). However, this research has generally involved short-term acute exposures with a small number of benthic species.

On the basis of their review and evaluation of the available approaches for the development of sediment quality values for Puget Sound, Tetra Tech (1986) selected five approaches (background, sediment-water equilibrium partitioning, sediment-biota equilibrium partitioning, screening level concentration and apparent effects threshold) as

meriting additional evaluation to assess their application in establishing sediment quality criteria values. The remaining approaches (water quality criteria, field bioassay, spiked bioassay) were not evaluated further, for the following reasons:

- water quality criteria are integrated into the sediment-water equilibrium partitioning approach;
- the field bioassay approach is considered as a part of the apparent effects threshold approach; and
- the spiked bioassay approach had not yet generated sufficient data to establish sediment quality criteria values.

4.3 Strategies for Developing Sediment Quality Objectives for Ontario

The review of available published and unpublished information, and the analysis and assessment of the MOE In-Place Pollutants Program database, has resulted in extensive tabular summaries of data on sediment toxicity, sediment-bioaccumulation relationship, sediment-benthic community structure relationships, and sediment release processes (Appendices 1 and 3). These tabulations provide a basis for guiding the development of strategies for deriving numerical sediment quality objectives by indicating the nature and amount of reliable information in the broad context, as well as indicating the feasibility of developing objectives for individual contaminants. For example, in the broad context, the amount of information available on sediment toxicity (lethal and sublethal), bioaccumulation, community structure effects and sediment release, as well as documentation of the types of tests or measurements that have been made, will define the total pool of available approaches that may be incorporated into rational and practical strategies for numerical sediment quality objectives development. The specific information available for individual contaminants will be used in determining any further data requirements before sediment quality objectives can be developed, based on strategies that are proposed. A feasibility matrix for applicability of the various approaches to development of sediment quality objectives for individual contaminants has been developed to aid in this process (Table 4.5).

Since the various approaches may lead to different criteria, it is advisable to apply as many approaches as available data permit in order to examine the 'robustness' of the final criterion adopted. In addition, it is possible to rank the various approaches in order

			Sediment (Quality Criteria	Development Ap	proach			
Contaminant	Background	Water Quality Criteria	Sediment- Water Partitioning	Sediment- Biota Partitioning	Water- Biota Partitioning	SLC	AET	Field Bioassay 1,2	Spiked Bioas sa v ¹
Arsenic	yes	yes	yes	yes	yes	yes	yes		
Cadmium	yes	yes	yes	yes	yes	yes	yes		-
Chromium	yes	yes	yes	yes	yes	yes	yes	yes yes	yes -
Copper	yes	yes	yes	yes	yes	yes	yes	ves	ves
Iron	yes	yes	yes	yes	yes	yes	yes	-	
Lead	yes	yes	yes	yes	yes	yes	yes		
Manganese	yes	yes	yes	yes	yes	yes	yes		
Mercury	ves	yes	yes	yes	yes	ves	yes		-
Nickel	yes	yes	yes	yes	yes	yes	yes		yes
Zinc	yes	yes	yes	yes	yes	yes	yes	yes	yes
Aldrin	yes	yes	yes	yes	yes	yes	yes	-	yes
a -BHC	yes	yes	yes	yes	yes	yes	yes	-	-
J-BHC	yes	yes	yes	-	-	yes	yes		-
γ-BHC	yes	yes	yes	yes	yes	yes) es	-	
a -chiordane	yes	-	-	-	-	yes	yes	-	
Դ -chlordane	yes	-	-	-	-	yes	yes	-	
oxy -chlordane	ves	-		-	-	yes	yes	-	-
Chlordane	yes	yes	yes	yes	yes	yes	yes		yes
o,p-DDT	yes	-	-	-	-	yes	ves	-	-
p.p-DDD	yes	-	-	-	-	yes	yes	-	
p.p-DDE	yes	-	-	-	-	yes) es		-
p,p-DDT	yes	-	-	-	-	yes	yes	-	yes
DDT	yes	yes	yes	yes	yes	yes	yes	-	
Dreidrin	yes	yes	yes	yes	yes	yes	yes	-	
Endrin	yes	yes	yes	yes	yes	yes	yes		yes
HCB	yes	yes	yes	yes	yes	yes	yes		
Heptachlor	yes	yes	yes	yes	yes	yes	yes		-
Heptachlor Epoxide	yes	-	-	-	-	yes	yes		-
Mirex	yes	yes	yes	yes	yes	yes	yes	-	yes
PCB	yes	yes	yes	yes	yes	yes	yes	-	yes

¹ yes' indicates bioassays in which a specific single toxic contaminant has been identified as eliciting the biological response

² field bloassay data exist for most contaminants if studies are used in which specific single toxic contaminants were not identified

of preference on a theoretical basis. A proposed order of preference, with supporting rationale, is outlined in this section.

A tiered approach to method selection is proposed, in increasing order of method preference, as follows:

- 1. Sediment Background
- Sediment-Water Partitioning, Sediment-Biota Partitioning, or Water-Biota Partitioning
- 3. Water Quality Criteria
- Screening Level Criteria (SLC), or Apparent Effect Threshold (AET)
- Field Bioassay, or Spiked Bioassay

In this scheme, the more empirical methods, and methods based on biological effect considerations, are preferred. Tier levels 2 through 5 all incorporate biological effect considerations in some manner, and are increasingly empirical. The value attributed to empirical approaches reflects the uncertainties associated with our understanding of the biological mechanisms involved and our ability to accurately predict biological effects from contaminant concentrations and simple coefficients.

With the sediment background approach, biological effects are not considered. However, background data are readily available, either from historical records or, more appropriately, from sediment core profiles. The greatest difficulty is in determining the most appropriate type of background data (e.g., tributary mouth or open lake areas; preagricultural or pre-industrial time horizons). These decisions are value judgements which depend on what we are trying to achieve by enforcing sediment quality criteria (i.e., how clean is clean enough? which benchmarks are appropriate in the absence of biological considerations?).

With the partitioning approaches (Level 2), sediment quality objectives are derived from water or biological tissue quality objectives by applying generic partitioning coefficients (e.g., $K_{\rm OC}$, BCF). Actual partitioning will vary considerably among sediment types and

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biological species, at least for some chemical parameters. The partitioning coefficients used should be as specific as possible to the sediments in which criteria will be applied, and the biota which criteria are designed to protect, as well as the specific contaminant under consideration. A particular problem here is that the water or tissue quality objectives will have been designed to protect different organisms (e.g., nektonic taxa or human consumers) than those meant to be protected by the derived sediment quality objectives.

Possibly sediment quality objectives derived from water quality criteria will prove to be conservative (i.e., lower than criteria based on benthic organism responses). However, generalizations of this nature are probably premature.

Tetra Tech (1986) rejected the sediment-biota partitioning approach because they did not find sufficient sediment-based bioconcentration data to validate the procedure. Certainly, bioconcentration studies have tended to focus on aqueous media. However, the database assembled during the present study appears to contain sufficient tissue and associated sediment data to derive preliminary sediment-based bioconcentration factors for many compounds. It may be that the extreme variability of such bioconcentration factors may limit their use, but this should be determined by analysis of the database.

The water quality criteria approach is similar to the sediment-water partitioning approach, with the important exception that empirical, site-specific relationships between sediment and interstitial water concentrations would be used in place of a generic $K_{\rm OC}$ value. For this reason, the approach is given a higher preference. It may be that the site-specific data confirm the applicability of the generic $K_{\rm OC}$ value. However, this confirmation increases the scientific defensibility of the approach.

The SLC and AET approaches (Level 4) are based entirely on empirical data concerning biological response to contaminant concentrations in sediments. They have a sound scientific basis and are highly defensible, and suitable data exist for most contaminants. They do depend, however, on a demonstrable response over a wide concentration range. Biological endpoints (e.g., presence/absence, density, diversity, mortality) which exhibit such a response can be selected, and also serve to explicitly define what is being protected by the resulting sediment quality objective.

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The data used to derive SLC and AET objectives are not confined to situations in which single specific contaminants eliciting the response have been identified. Thus, the great majority of field data will be suitable. However, existence or precision of the underlying dose response relatinships may be dependent on selection of studies in which the responsible toxicant(s) has (have) been measured.

The bioassay approaches (Level 5) are based on empirical biological responses to single specific toxicants known (or considered) to be eliciting the response. This is a difficult requirement to achieve in field studies, where it is primarily a question of suitable study site selection. It is generally achieved in laboratory (spiked bioassay) studies, although the costs associated with organism culture are high. Specific toxicant bioassay data are most highly preferred in generating toxicant-specific sediment quality criteria.

The input data needs and type of sediment quality objectives generated with the various approaches to criterion development are summarized in Table 4.6, along with the proposed tier level for each approach. Objectives derived by several different approaches should be compared prior to adopting a final value, and preference should be given to approaches in higher tiers. Consideration of hydrophobicity may also help to select the best approach for each contaminant.

The partitioning coefficients shown in Table 4.6 (e.g., K_{oC}) are appropriate for nonpolar organic contaminants. Sediment-water partitioning of inorganic contaminants and polar organics is less well understood. Consequently, there may be greater reliance on empirical dose response data and higher tier approaches. Sediment quality criteria development by the U.S. EPA for these two contaminant groups is not as well progressed as for nonpolar organic contaminants; however, the present intention is to consider similar approaches (Zarba, 1987).

All the approaches to criterion development discussed in this report are intended to generate contaminant-specific criteria, expressed in sediment concentration units. Chemical criteria are probably more easily enforced than criteria expressed in sediment toxicity units, since quality assurance procedures for the chemistry laboratory have been better defined and standardized. However, requirements for direct toxicity testing of sediments which fail to meet chemical objectives would seem to be a logical enforcement strategy, and sediment toxicity objectives could also be defined.

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				Sediment Qual.	Sediment Quality Criteria Development Approach	oment Approach			
	Sediment Background	Sediment-Water S Partitioning	Sediment-Water Sediment-Biota Partitioning Partitioning		Water Quality Criteria	SLC	AET	Field Bioassay	Spiked Bioassay
Proposed Tier	-	2	2	2		9	a	,	,
Input Data Needs	Background Concentrations	Background Water Quality oncentrations Criteria	Tissue Quality Criteria	Tissue Quality Criteria	Water Quality Doo-Lesponse Doo-Lesponse Criteria Relationship Relationship Relationship	Dos-response Relationship	Dose-response Relationship	Dose-response Relationship	Doxe-response Relationship
		8	BMF BCF _s (or BCF _{oc})	BCF. ⊗ A	Site-specific Interstitial Water Relationship				
Output Sediment Quality Objective	ž	C _{s/oc}	C _s (or C _{s/oc})	C _s /oc	C ₅ (or C ₅ /oc)	ű	రో	ນ້	บ้

 $[\]begin{aligned} & R_{\rm con} = 0 & \text{otherwise} \\ & R_{\rm con} = 0 & \text{otherwise$

Objectives for protection of aquatic life (and/or human consumers) are implicit in the derivation of numerical chemical objectives, and should dictate the type of input data used in those derivations (e.g., BCFs for appropriate species). Concurrent definition of explicit toxicity objectives would help to ensure a consistent focus in derivation of chemical objectives, and would also provide a means of determining whether the chemical criteria are achieving their purpose in specific cases.

A reasonable toxicity objective would be to ensure, as a minimum, that sediments are acutely non-lethal to benthic organisms which are prevalent in upstream or intake areas. ASTM has recently undertaken to develop suitable test procedures for sediments (Parrish, 1987). Organisms which might be used include amphipods, chironomids, oligochaetes, the odonate Hexagenia, or the sphaerid clam Pisidium.

A higher level of benthic community protection could be achieved by setting a toxicity objective of chronic non-lethality to organisms prevalent in upstream or intake areas. Examples of suitable tests include a ten-day chironomid growth test, in which long-term larval mortality, growth and morphological development can be monitored, or a 14-day amphipod growth test, in which long-term juvenile mortality and growth can be monitored. The highest level of protection is achieved by requiring that sediments have no sublethal effects on growth or development.

The level of benthic community protection desired is a value judgement made by society, and ultimately by the regulatory agencies.

4.4 Extent of the Database for Criterion Development

Sediment toxicity and bioconcentration data are reviewed in detail in Section 2.0. These data have been tabulated in a numerical database for use in criterion development. Examples of the database are provided in Appendices 1 and 3.

The database is estimated to be approximately 25% complete. Some key sources of outstanding data (particularly benthic macroinvertebrate community structure data) include the U.S. Corps of Engineers (Buffalo, Detroit, Chicago and St. Paul Districts), the U.S. EPA Large Lakes Research Station (R. Kreis), MOE Connecting Channels and In-Place Pollutants Program data, and unpublished data from D.S. White (University of

Michigan). However, the data tabulated so far are considered representative, and sufficient in quantity to indicate which contaminants and types of data are best represented.

The types of data required for development of sediment quality criteria, following the approaches outlined in Section 4.2, include corresponding water and sediment concentrations for determination of sediment-water partitioning coefficients, corresponding sediment and tissue concentrations for determination of bioconcentration factors, and corresponding sediment concentrations and toxic effects on benthic species (LC50) or communities (density, diversity). The distribution of data by type and contaminant is shown in Table 4.7.

Most of the data in the database pertains to heavy metals in sediments. Copper, mercury and cadmium are best represented, with over 200 samples of each in the database. Most other metals (arsenic, chromium, iron, manganese, nickel, lead and zinc) are represented by at least 100 samples. Approximately 60% of the metal concentrations are associated with corresponding water concentrations, while approximately 10% are associated with corresponding tissue concentrations. The same proportion (approximately 10%) are associated with toxic effects of some kind. The database includes sediment-based LC50 concentrations for copper, cadmium and zinc, and benthic density and diversity observations for all metals except arsenic, each associated with approximately 10% of the sediment-metal concentrations.

Persistent organic contaminants in the database are represented primarily by PCB, DDT, DDE and dieldrin, in decreasing order of frequency from 64 samples (PCB) to 29 samples (dieldrin). Other pesticides are represented by fewer than 20 samples each. Sediment concentrations are associated with corresponding water concentrations only for PCB. Corresponding tissue concentrations of PCB, DDT, DDE, dieldrin, endrin, heptachlor, DDD and γ -BHC are included in the database. Toxic effects are reported in association with all organic contaminants except γ -BHC; however, no LC50 concentrations or benthic community responses are reported.

While numerous database entries contain both toxic effects and chemical concentrations in sediments, few identify the chemical measured as definitely responsible for the observed effect (i.e., as in single contaminant studies). There are 44 such entries for

			Percenta	ge of Da	Percentage of Data Entries with Each Type of Data	ch Type of Da	ta	
Chemical Parameter	No. of Cases	Significant Toxic Effect	Water Concentration	LC50	Tissue Concentration	Benthic Density	Benthic Diversity	Concentration Range (ug/g)
As	103	7,77	6.69	0	6.80	0	0	2-65
PO	509	13.9	34.4	10.5	13.9	9,57	7.18	0.1-40,000
Ď	157	17.2	39.4	0	5,73	12.7	9.55	2.6-2,129
, O	27.0	19,6	55.9	20.0	5.19	28.9	16.7	9-10,600
Fe	117	6.84	73.5	0	7,69	8,55	7.69	226-90,500
Hg	218	7.80	45.8	0	28.0	9,17	6.88	0.03-684
Mo	117	6.84	7,95	0	6.83	8.55	7.69	16.2-1,800
ï	130	14.6	27.7	0	0	15.4	11.5	6-350
Pb	17.3	14.5	35,3	0	19.7	11.6	8.67	0,59-3,640
Zn	196	14.3	36.7	1.02	6,63	10.2	7.65	0.5-17,300
Aldrin	01	0.04	0	0	0	0	0	L* 0.08-1,000
Chlordane	13	38.8	0	0	0	0	0	1 0,00-1,000
Dieldrin	53	6.90	0	0	72,4	0	0	L 0.00-0.01
Endrin	18	22.2	0	0	27.8	0	0	L 0.00-1,000
HCB	9	33.3	0	0	0	0	0	L 0.08
Heptachlor Epoxide	9	33,3	0	0	0	0	0	T 0.00-L 0.08
Heptachlor	14	14.3	0	0	50.0	0	0	T 0.00-0.08
PCB	49	15.6	14.1	0	32.8	0	0	L 0.01-31.72
a-BHC	9	33,3	0	0	0	0	0	L 0.00-L 0.08
β-BHC	9	33,3	0	0	0	0	0	T 0.00-L 0.08
7-BHC	×	0	0	0	87.5	0	0	T 0.00-L 0.00
DDD	∞	25.0	0	0	25.0	0	0	L 0.00-0.04
DDE	04	5.0	0	0	50.0	0	0	L 0.00-0.08
DDT	47	8.5	0	0	14.5	0	0	0.00-1,000
Mirex	ħ	100.0	0	0	0	0	0	5-1,000

* L = less than.

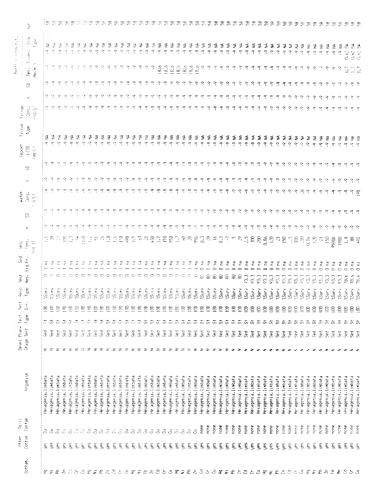
copper, 12 for cadmium, four for mirex, and two each for zinc, DDT, endrin, chlordane and aldrin. Therefore, any dose-response relationships derived from the database as a whole are likely to be 'noisy' and, with small numbers of samples, there is a danger of spurious relationships appearing. The quantity of data for heavy metals is likely large enough to guard against such spurious relationships; however, much more data will be needed for most of the organics. There may be sufficient data at present for PCB (N = 64). Tetra-Tech (1986) used from 30 to 60 data points in derivation of each sediment quality objective, using the methods outlined in Section 4.2.

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APPENDIX 1

Example of Sediment Toxicity Database

Benthuc Comunity



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APPENDIX 2 Toxicity of Waterborne Contaminants

Favor	sarsads	Type of 29th 98th 96th Test LC50 LC50 LC50	29-lin 98-lin 96-lin Linso Linso D	48.hr LC 50	96-br	Other*	ype of 25de 98de 96de Tect LCCO LCCO LCO Other* Bennarks	Peference
Cristicea, Amphipoda	Gammans pendoliminens G. peudolimiaeus G. pendolimiaeus G. peudolimiaeus			g	1,90 0,874	1,02 0,088 0,961 0,973	- 72the LCS0, Av ² ; Hardwes : 48 mg/L - 14-4 8 5%, survival; Av ² ; Hardwes : 40 mg/L - 14-4 60%, survival; Av ² ; Hardwes : 40 mg/L - 14-4 80%, survival; Av ² ; Hardwes : 40 mg/L	Lima et al. (1984) Spehar et al. (1980) Spehar et al. (1980) Spehar et al. (1980)
Insecta, Plecoptera	Pteronarrys dorsatu P, dorsata	L L				0,961	* 28-d 100% survival; As 3 ; Hardness = 44 mg/L * 28-d 100% survival; As 3 ; Hardness = 44 mg/L	Spehar et al. (1980) Spehar et al. (1980)
Molluwa, Gastropeda	Helisoma campanulata H. campanulata Stagnicola emarginata S. emarginata					0,961 0,973 0,961 0,973	22cd 95% surevival; A3 ² ; Hardness = 48 mg/L • 28cd 95% surevival; A3 ² ; Hardness = 94 mg/L • 28cd 100% surevival; A3 ² ; Hardness = 94 mg/L • 28cd 90% surevival; A3 ² ; Hardness = 44 mg/L	Spehar et al. (1980) Spehar et al. (1980) Spehar et al. (1980) Spehar et al. (1980)

F - flow-through; S state.

APPENDIX TABLE A2.2: TOXICTIY OF WATERFORMEC ADMICM TO BENTHE MAC POINTER BRATES

			,	oor entr	Concentration (ing/U)	(0)		
T-a x con	Species	Type gl	29-br Lt. 50	48.hr Lt 50	76-hr LC 50	Other.	Remarks	Reference
Coelenterata	Bydea littoralis	v				0.020	• 6-12 d subjetbal threshold concentration; Hartness 70 mg/L	Santiago-Fandino (1983)
Platyletminthes, Tricladia	Polycelis tenus	_	570	125	7.0		Hardness 152 mg/L	Williams et al. (1985)
Annelida.	Peanchura sowerbyi	,	,	,	0.24		Hardness a 5 mg/l	Chapman et al. (1982a)
Ole ochaeta	B. sowerbyi	9			2		With substrate: Hardness - 5 mg/L	Chapman et al. (1982a)
	I innodrilus hoffmeisteri	_	24	6.4	2,4		Hardness 152 mg/l.	Williams et al. (1985)
	L. hoffmersteri	~			0.17		Hardness - 5 mg/L	Chapman et al. (1982a)
	L. hoffmeisteri	s			3.5			Chapman et al. (1982a)
	Nais sp.	,	ý,		7		Hardness 50 mg/L	Rehwoldt et al. (1973)
	Quistadrilus multisetnsus	'n			0.32		Hardness - 5 mg/L	Chapman et al. (1982a)
	Q. multisetosus	, ·			7.4		With substrate; Hardness - 5 mg/L	Chapman et al. (1982a)
	Rhyacodrillus montana	s)			0,63		Hardness - 5 mg/L	Chapman et al. (1982a)
	Spirosperma nikolskyi	л :			0.40		Hardness - 5 mg/L	Chapman et al. (1982a)
	S. nakolskyi	r			12.0		With substrate; Hardness: > mg/L	Chapman et al. (1982a)
	S. ferox	· ·			0,35		Hardness 5 mg/L	Chapman et al. (1982a)
	Stylodrilus heringianus	٠.			0.5			Chapman et al. (1762a)
	S. beringianus	e :			9		With substrate; Harchess > mg/L	Chapman et al. (1982a)
	Total Contex	٠.			7.0		transfers 2 mg/L	Chapman et al. (1962a)
	1. tubilex	, ,	. 00 0	. 000	£.8		0000	Chapman et al. (1782a)
	I. tabilex	^	0,001	0,0017 0,0028			Hardness 0,1 mg/L	firkovic-Popovic and Descrip (1977a)
	T todofex	v	0.06.3	0.00			Hardware Manuell	Behovic-Donovic and
	·		3	0.0				Popovic (1972a)
	T, tubifex	5	1.20	0,72			Hardness 261 mg/l.	Brkovic-Popovic and
								Popovic (1977a)
	Varichaeta pacifica	S			0, 38		Hardness = 5 mg/L	Chapman et al. (1982a)
	L. hoffmersteri/T. tubifex	v.			0,58		Hardness - 5 mg/l.	Chapman et al. (1982b)
Crustairea,	Ase flus aquations	S		4, 58	1.32		Hardness 50 mg/L	Martin and Holdich (1986)
Propoda	A, aquaticus	۷			G ² 1,750		Embryo Stage V. Hardness 10 5 mg/L	Green et al. (1986a)
	A. aquaticus	_		,	0.240		Embryo Stage D'; Hardness - 105 mg/L	Green et al. (1986a)
	A. aquaticus	۷			0.053		Juvenile: M.L. 1.35 mm; Hardness - 105 mg/L	Green et al. (1986a)
	A. aquatims	L			0.150		Juvenile: M.L. 1.60 mm; Hardness : 105 mg/l.	Green et al. (1986a)
	A. aquaticus	L. 1			0.170		Juvenile: M.L. 2, 40 mm; Hardness = 10.5 mg/L	Green et al. (1986a)
	A, aquaticus	L .			0.230		Juvenile: M.L. 3.52 mm; Hardness = 105 mg/L	Green et al. (1986a)
	A aquations	i (-			0.430		Adult: Hariness - 105 mg/L Adult: Hariness - 105 mg/L	Green et al. (1986a)
	A aguaticus				200		Soft water	Slow (F (1983b)
	A. aquaticus	- 1-	=	3.6	9,0		Hardness - 152 mg/L	Williams et al. (1985)

APPINDIX TABLE A2.2: TOXICITY OF WATERFORME, CADMIN'M TO BEN'THIC MACROINVERTERPATES

				oncentr	Concentration (mg/L)	(1)		
Taxon	Species	Type of Text	24-hr 1 C 50	48-hr 21, 50	96-hr	Other	Remarks	Reference
Crustacea,	Crangonyx pseudogracilis	v		34.6	1.70		Hardness = 50 mg/L	Martin and Holdich (1986)
Amphipoda	Gammarus pulex	S		0.08		,	Soft water	Stooff (1983b)
	G. pulex	la,	4.	0,4	0,02	ı	Hardness = 152 mg/L	Williams et al. (1985)
	G. pulex	0		0,68	0.12		5	Wright and Fram (1981)
	Gammarus sp. Hyallela azteca	<i>r</i> L			0,008	1, 0,0028	* 10-d LC50; Bardness = 34 mg/L	Nebeker et al. (1984a)
Crustacea,	Cambarus latimanus	[iiu			,	0,005-	 5 mos critical toxicological level 	Thorp et al. (1979)
Decapoda						0.010	1) N	Managed (1986a)
	Orconectes virilis	- 1			2	0.0	* 10 4 L 50 Hardness : 20 mg/L	Mirenda (1986a)
	O. virilis	_ 1				0.20	• 14 d f C 50 Hardness - 26 mg/L	Mirenda (1986a)
	O variants	- 1			C 10.2		Hardness : 44 mg/L	Phipps and Holcombe (1985)
	Decreebberre clarks	. 0			5 85		Temperature - 20°C: Hardness - 240 mg/l	Del Ramo et al. (1987)
	D clarkii				34.8		Temperature : 24°C: Hardness : 240 mg/L	Del Ramo et al. (1987)
	P. clarku	1 1/2			8.4		Temperature = 28°C; Hardness = 240 mg/L	Del Ramo et al. (1987)
								(0.000)
Insecta,	Chronomus tentans	s				50	• LD100	Rathore et al. (1979)
Diptera	C, riparius	L			300		Hardness = 152 mg/L	Williams et al. (1982)
	C. riparius	v	7.			325	 10-hr LC 50; 1st instar; Hardness = 102 mg/L 	Williams et al. (1986)
	C. riparius	v	260	5	- :	1,350	• John LC XV; And Instant; Handness = 102 mg/L	Williams et al. (1986)
	C, riparius	<i>s</i>	000	7/	77	007*7	I During EC 20g and invitating than caness is 10.3 mg/L	Williams of all (1984)
	C, riparius	^ .	000.	177	5 .	2,100	TOTAL DE JOS AND JUSTICAL PROFINESS = 100 mg/L	Debuolds of all (1973)
	Chronomus sp.	0	7.		7.7	80.00.0	* Doe to 2nd or 3rd metaer bland = 47 me/1	Anderson et al (1980)
	Tany far sus dissimitis	^		,		0,110 8	CAR TO AND OF MA INSCALL, MAINLY TO THE L	Constant and Constant
Insecta.	Leuctra mermis	LL.	700	8.2	3.2		Hardness 152 mg/L	Williams et al. (1985)
Flecoptera	Acronentia lycorias	S				35	 14-d LC 50; Hardness = 52 mg/L 	Warnick and Bell (1969)
	Pteronarcella badia	1			×	,	Alkalinity = 240 mg/L	Clubb et al. (1973)
Insects	Hydroneyche aneustineous	1	,	,	520		Hardness = 152 mg/l.	Williams et al. (1985)
Truchontera	H herren	v			1	32.0	 10-4 LC 50; Hardness = 56 mg/L 	Warnick and Bell (1969)
and and and	Prachycentrus americanus	-				42.5	 10-d 100% survival: Alkalınıty = 240 mg/l. 	Clubb et al. (1975)
	Unidentified sp.	v.	7.		3.4	,	Hardness = 50 mg/L	Rehwoldt et al. (1973)
								0.000
Insecta, Odonata	Indentified sp.	~	0.	,	ž.		Hardness = X0 mg/L	Rehwoldt et al. (1971)
hsecta,	Ephemerella subvaria	S		,	2,0		Hardness - 54 mg/L	Warnick and Bell (1969)
Ephemeroptera	I. grandis	L			28	,	Alkalınity - 240 mg/l.	Clubb et al. (1975)
	F. ignita	<u>_</u>	2	œ.	Ξ		Hardness - 152 mg/L	Williams et al. (1985)
	Ephemerella sp.	L				L 0,003	 28-d LC 50; Hardness - 45 mg/l. 	Spehar et al. (1978)
	Rietis rhodani	_	06	ə	6.0	,	Hardness = 152 mg/L	Williams of all (1980)

APPININX TABLE A2.2: TOXICLEY OF WATERFORMS CADMISM TO BUILDING MACRONING RELIGIOUS

	Reference	Hotcombe (1984)	Physys and Holcombe (1983) Rehwoldt et al. (1973) Rehwoldt et al. (1973) Williams et al. (1983) Wire and Willer (1986) Wire and Whiter (1986)
	Remarks	• MATC ⁴ ; Hardness 45 mg/L	Hardness 94 mg/l. Fggrt Hardness 90 mg/l. Adult't Hardness 30 mg/l. Hardness 125 mg/l. Juvensle; Hardness 200 mg/l. Adult; Hardness 200 mg/l.
3	Type of 24-hr 48-hr 96-hr Test LC50 1C50 1C50 Other*	0,00250.	0,0104
(one entration (mg/t)	%-hr F. 50	0,093	2,8 2,8 2,8 1,37 1,37
one entr	48.hr 1 < 50		
,	24-br LC 50		2.05.2
	Type of Text	L	FAAFAAF
	sur ads	Aplexa hypnorum	A, hyprerum Amarcola sp. Amercola sp. Physa fontinalis P. gyrtna P. gyrtna P. mtegra
	Treen	Mollusca, Gastropoda	

² G. greater than.

¹ F flow-through; S : static.

³ L. fess than,

 $^{^{\}hat{q}}$ MATC - maximum allowable toxicant concentration,

APPENDIX TABLE A2.3: TOXICITY OF WATERBORNE CHROMITM TO BENTHE WACROINVERTERRATES

			0	oncentr	Concentration (mg/L)	(1)		
Taxon	Species	Type of Test	24-hr LC 50	48.hr LC50	96-hr LC 50	Other.	Remarks	Reference
Annelida,	Tubifex tuhifex	S	0.088	0,063		,	Cr 6+; Hardness - 0,1 mg/L	Brkovic-Popovic and Popovic (1977a)
Oligorhaeta	T. tubifex	un u	13.	200			Cro.; Hardness = 34 mg/L	Brkovic-Popowic and Popowic (1972a)
	Nats sp.	o s	12.1	9	5	,	Cr 3.; Hardness - 50 mg/L	Rehwoldt et al. (1973)
Crustacea, Isopoda	Asellus aquaticus	v		437	442		Cr ³⁺ ; Hardness = 50 mg/L	Martin and Holdich (1986)
Crustacea.	Crangonyx pseudogracilis	s	,	38.8	29.1		Cr, 3+; Hardness = 50 mg/L	Martin and Holdich (1986)
Amphinoda	C. pseudograculis	S	,	5.69	0.81	,	Cr**; Hardness = 50 mg/L	Martin and Holdich (1986)
	C. pseudogracilis	s		2.20	0.42		Cr. Hardness = 10 mg/L	Martin and Holdich (1986)
	Gammarus sp.	S	6.4	·	3.2		Cr ** Hardness = 50 mg/L	Rehwoldt et al. (1973)
Crustacea, Decapoda	Procambarus clarkii	S	,	,	G ² 500		Cr ⁶⁺ ; Hardness = 180-300 mg/L	Del Ramo e <u>t al.</u> (1987)
Inserta, Diptera	Chironomus sp.	s	16.5	,	0.11	,	Cr3+; Hardness = 50 mg/L	Rehwoldt et al. (1973)
Insecta, Plecoptera	Acroneuria lycorias	v				32.0	Cr ³⁴ ; Hardness = 50 mg/L	Warnick and Pell (1969)
losects	Hydronsyche betten	V	,	,	24		Cr. 1: Hardness - #2 mg/L	Warnick and Bell (1969)
Trichoptera	Undentified sp.	S	28	,	20		Cr 3+; Hardness - 50 mg/L	Rehwoldt et al. (1973)
Insecta, Odonata	Indentified sp.	S	949		43.1		Cr ³⁴ ; Hardness - 50 mg/L	Rehwoldt et al. (1973)
Insecta, Ephemeroptera	Ephemerella subvaria	s			2,0		Cr ³³ ; Hardness - 50 mg/L	Warnick and Rett (1969)
Molluwa, Gastropoda	Amnicola sp. Amnicola sp.	SS	15.2		12.4		Cr 14; Eggs; Hardness - 50 mg/L Cr 14; Adult; Hardness + 50 mg/L	Rehwoldt et al. (1973) Rehwoldt et al. (1973)

F. flow-through; S. static.

2 c. sgreater than,

			_	oncentr	Concentration (mg/L)	(1/)		
Taxon	Species	Type of Test	24-hr LC 50	48-hr LC50	96-hr LC 50	Other.	Remarks	Reference
			9	000				4
Annelida,	Fubilix tubilex	^	0.010	0,0064	,	ı	Hardness = 0,1 mg/L	Brkovic-Popovic and Popovic (1977a)
Oligochaeta	r. tubilex	^	96.0	0.21			Hardness = 54 mg/L	Bekovic-Popovic and Popovic (1977a)
	i. tubilex	0	. 38	6.84	, 0	,	Hardness = 261 mg/L	Erkovic-Popovic and Popovic (1977a)
	Nais sp.	^	6.3		60.03		Hardness 2 20 mg/L	Rehworldt et al. (1973)
Crustacea, Isopoda	Asellus aquaticus	N			9,21		Hardness = 50 mg/L	Martin and Holdich (1986)
Orustarea,	Crangonyx pseudogracilis	S	,	2.44	1.29		Hardness = 50 mg/L	Martin and Holdich (1986)
Amphinoda	Gammarus fasciatus	S	,	0.2	,		Hardness = 200 mg/L	3ndv (1979)
	G. pseudolimnaeus	ښنا	,	í	0,02	-940000	• NOEL based on one generation	Arthur and Leonard (1970)
						0,000	cybosaic; naraicss - 42 mg/L	
	G. pulex G. pulex	s s	0.086	0.041	0.021	0,030	 72-hr LC 50; Hardness = 104 mg/L 72-hr LC 50; Hardness = 249 mg/L 	Stephenson (1983) Stephenson (1983)
	Gammarus sp.	S	1.2	í	16.0		Hardness = 50 mg/l.	Rehwoldt et al. (1973)
brects Dinters	Chironomus decouse	,		0.739			4th instar- Hardness - 40-58 mg/l	Kosalwat and Knieht (1987b)
manded the con-	C tentility	10			16.7		let instarr soft water	Cause et al (1985)
	C. tentans	r			36.5		1st instar: medium water	Gauss et al. (1985)
	C. tentans	٥	,	,	98.2	,	1st instar; hard water	Gauss et al. (1985)
	C, tentans	6	,	,	211	,	4th instar: soft water	Gauss et al. (1985)
	C. tentans	c	,	,	226	,	4th instar; medium water	Gauss et al. (1985)
	C. tentans	6	,	,	1.184	,	4th instar; hard water	Gauss et al. (1985)
	C, tentans	ш	,		0,298	,	1st instar; Hardness - 71 mg/L	Nebeker et al. (1984)
	C. tentans	la. i	,	0,608	. :		2nd instar; Hardness = 26 mg/L	Nebeker et al. (1984)
	C, tentans	L I			3,73	,	2nd instar; Hardness + 84 mg/L	Nebeker et al. (1984)
	C tentans	_ L			1 446		And instant, Hardwess - 21 mg/L	Nebeler of at (1984)
	C tentans	_ 1_		0 1 366			9th instart Bardness - 26 mg/L	Nebeler et al. (1984)
	Clentans					6.0.529	*12.4 10 30- 9th instar- Hard - 30 mg/l	Nebeker et al. (1984)
	C. tentans	. 12.			G 0.467	0.0775	*20-d LC 50: 4th instar: Hard. = 36 mg/l.	Nebeker et al. (1984)
	C, tentans	la.	,	,	1.690	,	4th instar; Hardness - 84 mg/L	Nebeker et al. (1984)
	C. tentans	Ŀ	,			0,0775	*20-d LC 50; 4th instar to adult	Nebeker et al. (1984)
							emergence; Hardness - 36 mg/L	
	Chironomus sp.	vi s	0.65	,	0.03	, 5	Hardness - 50 mg/L	Rehwoldt et al. (1973)
	Faratanytarsus	^				0.37	"I week exposure 20% reproductive	Hatakeyama and Yasuno (1981)
	Tany tarsus dissimilis	s	,		,	0.0163	*Egg to 2nd or 3rd instar; Hardness = 47 mg/L	Anderson et al. (1980)
bracts	Disconnector collifornico					0	110 d 147 th Hardware 30 70 mm/l	Neterina (1927)
Plec optera	Acronentia lycorias	ıvı			. 6%		Hardness : 40 mg/L	Warnek and Rell (1969)

ADDITIONAL TABLE ASS. TOXICLITY OF WATERBORNE COPPLETO BENTHE MAC ROUNDER FEBRATES.

	Reference	Nebeker et al. (1984c) Warnick and Bell (1969) Rebwoldt et al. (1973)	Rehwoldt et al. (1973)	Nehring (1976) Warnick and Bell (1969)	Rehwoldt et al. (1973) Rehwoldt et al. (1973) A flux and Levinat (1973) Nebeler et al. (1986b) Arthur and Levinat (1970)
	Pemarks	*NOFL for 3 generation life cycle test; Haerless, 26 mg/L *Ple-at LC 50; Hardeess * 46 mg/L Hardness * 50 mg/L	Hardness = 50 mg/L	*14-d LC 50; Hardness 30-70 mg/L Hardness = 40 mg/L	Hardness - 30 mg/L Hardness - 30 mg/L Caerde, exposure NOEL; Hard 45 mg/L '93-d COG; Hardness - 21 mg/L '93-d COG; Hardness - 23 mg/L '93-d COG; Hardness - 23 mg/L '93-d COG; Hardness - 21 mg/L '63-d COG; Hardness - 21 mg/L '63-week, exposure NOTI; Hard 45 mg/L
5	Other	12.0		0.18.0.20	0.098-0.0148 14 0.008 0.006 0.007 1. 0.008 0.008-
Concentration (mg/L)	96-be Lc 50	6.22	4.6		9,3 0,9 1,7 0,015 - 0,008 0,008
oncentr	24-hr 48-hr 96-hr LC 50 LC 50 LC 50			0.12	
			10,2		35
	Type of Text	~ ~ ~	v	V V	××=======
	satuds	Clistorana magnifica Hydropsyche hetten Undentified sp.	Unidentified sp.	Ephemerella grandis F. subvaria	Ammerola sp. Ammerola sp. Campeloma derisum Juga plicitera 2. plicitera Lithogiyphus virens Li, virens Physa integra
	Lave	Invecta, Trichoptera	Ince ta, Odonata	Insecta, Ephemeroptera	Mollusea, Gastropola

¹ F. flow-through; S. static.

² NOTE - ro-observed-offect level.

 $^{^3}$ G. greater than, 4 L. less than,

APPI MOLY TABLE A2.5. TOXIC 1PY OF WATERIODNE IRON TO BENTHE MACROINVER TEMPATES

			Ĭ	oncentr	(oncentration (ng/I)	(1)		
laxon	Shed her?	Type of Test ¹	~ -	29-hr 48 hr 96-hr 1C50 1C50 LC50		Offier*	Pemarks	Reference
				1				
constacta,	Avelles aquations	_		8	57		Fe 1; Hardness - 50 mg/L	Martin and Holds b (1984)
Dopoda	A, aquaticus	S				255.9	*\$2-br LC 50; Fe ²⁷ ; pH 4.6	Maltby et al. (1987)
	A, aquaticus	<i>y</i>				18.1.2	*52-br I C 50; Fe ²⁺ ; pH 4.6; previously expoyed animals	Maltby et al. (1987)
	A. aquaticus	٧				4.10.5	*52-hr I C 50; Fe ^{2*} ; pH 6,5	Maltby et al. (1987)
	A, aquations	~				6794	• 52-hr LC 50; Fe ^{2 ±} ; pH 6. 5; previously expowed animals	Maltby et al. (1987)
Cristacea,	Crangonyx pseudograculis	V		177	95.0		Fe ^{2*} ; Hardness - 50 mg/t.	Martin and Boldich (1986)
Amphipoda	C. peudigracuis	s		091	2		Fe 1.; Hardness 50 mg/l	Martin and Holduch (1986)
Insecta, Plecoptera	Acroneuria Iyrorias	v				16.0	*9.d LC 50, Fe ^{2*} ; Hardness - 48 mg/L	Warnick and Bell (1969)
Insecta, Trichoptera	Hydropsyche betten	v				16,0	•7d LC 50; Fe ^{2*} ; Hardness - 50 mg/l.	Warnick and Bell (1969)
fasecta, Ephemeroptera	Ephemerella subvaria	v			0, 12		Fe ²⁺ ; Hardness + 48 mg/l	Warnick and Bell (1969)

F flow-through; 5 static.

	Reference		T. Martin and Holdie'h (1984)		T. Martin and Holdich (1986)	sess = 45 mg/L Spehar et al. (1978)	Pathore et al. (1979)	Egg to 2nd or 3rd instar; Hard, = 47 mg/L Anderson et al. (1980)	Warnick and Bell (1969)	ness = 30,70 mg/L Nebring (1976)	We significant mortality after 28 d; Spekar $\underline{c}_1 \underline{a}_L$ (1978) 4 ardness = 45 mg/L	*No significant mortality after 28 d; Spehar et al. (1978)		rss - 59 mg/l. Warnick and Bell (1969)	=10-d LC50; Hardness = 30-70 mg/L Nehring (1976)	iess = 52 mg/L Warnick and Bell (1969)	Special 29 4.
	Remarks		Hardness = 50 mg/L		Hardness = 50 mg/L		.15100		* 14-d LC 50; Hardness = 54 mg/L	*14-d LC50; Hardness = 30-70 mg/L				•7.d LC 50; Hardness - 59 mg/L	• I4-d LC50; Hardr	• 7-d LC 50; Hardness : 52 mg/L	this conficus amountains of the
27.77	Other.					0.0284	20	0.258	G2 64.0	G 19.2	0,56.5	0,565		12.0	5	16.0	0
100	96.hr		1.49		27.6	0,124				,							
College and Telegraphy	48.4		120		43.6									1	,	,	
	24-hr	2	1								•						
	Type of Toyal		v		v	v	V	v	v	v	v	v		v	V	v	u
	de contract	Shorts	Asellos aquaticus		Cramanow proudoerscule	Gammarus pseudolimnaeus	Chironomus tentans	Tanytarsus dissimilis	Acronouria lycorias	Pteronarcys californica	P. californica	Bracharentris so.		Hydropsyche hetteni	Ephemerella grandis	E, subvaria	
		18400	Criistacea,	Tropoda	Constitution	Amphipoda	hweta, Diptera		Invecta,	Plecoptera		Insects	Trichoptera		Inweta,	Ephemeroptera	

¹ E - flow-through; S - static, ² G - greater than,

APPENDIX TABLE A2.2: TOXICITY OF WATERBORNE MANGANESE TO BENTHIC MACROINVERTERRATES

			C	oncentra	Concentration (mg/L)	70		
		Type of 24-hr 48-hr 96-hr	24-hr	48-hr	96-hr			
Taxon	Species	Test	LC 50	LC 50	LC 50	Other •	LC50 LC50 LC10 Other* Remarks	Reference
Crustacea, Isopoda	Asellus aquaticus	~		771 333	33		Mn ² '; Hardness = 20 mg/L	Martin and Holdich (1986)
Crustacea, Amphipeda	Crongonyx pseudogracitis C. pseudogracitis	v. vs	1 1	1,189 694 0,99 0,50	969		${\rm Mn}^{2}$; Hardness = $50{\rm mg/L}$ ${\rm Mn}^{7}$; Hardness = $50{\rm mg/L}$	Martin and Holdich (1986) Martin and Holdich (1986)
F = flow-through; S = static.	gh; S = static.							

w-through; > : static.

APPENDIX TABLE A2.9. TOXICITY OF WATERDRIN NECT. TO BENTHE MACROINVERTERING

			Ĭ	ose entr	Concentration (mg/L)	(1)		
Гакон	Species	Type of Tret	24.hr	48.ler Et 50	96.hr LC 50	Other*	Remarks	Reference
Coelenterata	Hydra Intoralis	~				0.075	•6-12 d subjethal threshold concentration; Hardness = 70 mg/L	Santiago-Fandino (1983)
Ametida, Ottgochaeta	Nass sp. Tubsfex tubsfex T. tubsfex T. tubsfex	~~~	16.2 0.12 33.4 120	0.082 8.70 61.4	<u>.</u>		Hardness 30 mg/L Hardness 10,1 mg/L Hardness 34 mg/L Hardness 28 mg/L	Rehwoldt et al. (1973) Pkkovic-Popovic and Popovic (1977a) Brkovic-Popovic and Popovic (1977a) Brkovic-Popovic and Popovic (1977a)
Crustarea, Isopoda	Asellus aquaticus	×		435	611		Hardness - 50 mg/L	Mar tin and Holdich (1986)
Crustacea, Amphipoda	Crangonyx pseudogracilis Gammarus sp.	v v	15,2	252	13,0	4.1	Hardness = 50 mg/L Hardness = 50 mg/L	Martin and Holdich (1986) Rehwoldt et al. (1973)
hierta, Diptera	Chironomus riparis C. riparis C. riparis Chironomus sp.	~~~ ~	10.2	169		5	1st instar; Alkalinity - 210 mg/L. 2nd instar; Alkalinity = 210 mg/L. • MATC* based on egg to prior to pipation (30 days) exposure; Alkalinity = 237 mg/L. Blanchess = 50 mg/L.	Powlesland and George (1986) Powlesland and George (1986) Powlesland and George (1986) Rehwoldt et al. (1973)
Insecta, Plecoptera	Acroneuria lycorias	v.			33.5		Hardness - 40 mg/L	Warnick and BeJI (1969)
losecta, Trichoptera	Clistoronia magnifica Hydropsyche betteni Unidentified sp.	L 0.0	4.8		C. 3 37	0.046 G 64.0	*NOFL 4 for 3 generation life cycle test; Bardness - 34 mg/L *19-d LC 59; Bardness - 48 mg/L Bardness - 30 mg/L	Nebeker <u>et al.</u> (1984c) Warnick and Bell (1969) Rehwoldt <u>et al.</u> (1973)
Insecta, Odenata Insecta,	Uoidentified sp. Ephemerella subvaria	v v	8.9		21.2		Hardness - 50 mg/L. Hardness = 42 mg/L.	Rehwoldt <u>et al. (</u> 1923) Warnick and Pell (1969)
Mollusca, Gastropoda	Amnicola sp. Amnicola sp. Juga plicifera J. plicifera Physa gyrina	~~~~	26.0		11.4 14.3 0.237 0.239	0,204	Egg: Hardrevs = 30 mg/L. Adult; Hardress = 30 mg/L. Adult; Hardress = 39 mg/L. *30-d NOEL; Hardress = 39 mg/L. Hardress = 26 mg/L.	Rehwoldt <u>et al.</u> (1973) Rehwoldt <u>et al.</u> (1973) Nebelser <u>et al.</u> (1986) Nebelser <u>et al.</u> (1986) Nebelser <u>et al.</u> (1986)

[|] F - flow-through; \$ > static, AMTC = maximum allowable toxicant correntation, | G greater than, | NOTL = no-abserved-effect level,

APPLINIX TABLE A2.10: TOXK ITY OF WATERBORNE ZINC TO BENTHIC MACROINVIPTEBRATES

	Remarks		Hardness = 50 mg/L Martin and Holdich (1986)	Hardness = 30 mg/L Martin and Holdreh (19%e) Hardness = 30 mg/L Rehwoldt et al. (1973)	*2-wrisk LC50; Hardness = 26 mg/L Mirenda (1986b)	Hardness - 50 ng/L Trgs to 34d or Yed Matar, Hardness - Anderson et al. (1930) Anderson et al. (1930)	*19.d LC50: Hardness = 30 mg/L Warmck and Bett (1969)	**************************************	cost characters - 32 mg/L Warnick and Bell (1969) 11-d 10-050 kmg/L Rehwoldt et al. (1973) Hardness = 50 mg/L	Hardness = 50 mg/L Rehwoldt et al. (1973)	116-d LC 30; Hardness - 30-70 mg/L Nehring (1976) 10-d LC 30; Hardness - 30-70 mg/L Warnick and Bell (1969) 116-d LC 30; Hardness - 30-70 mg/L Nehring (1976)	Eggs Hartness - 10 mg/L Rehwoldt et al. (1973) Adult; Hardness - 10 mg/L Rehwoldt et al. (1973) Adult; Hardness - 16 mg/L Nebsker et al. (1984a)
	Remarks	Hardress = 50 mg/L Hardress = 0.1 mg/L Hardress = 30 mg/L Hardress = 261 mg/L	Hardness = 50 mg/L	Hardness = 50 mg/L Hurdness = 50 mg/L	*2-wrok I.C50; Hardness	Hardness - 50 mg/L *Egg to 2nd or 3rd instar;	*14.d LC50; Hardness : 5	*NOTL for 3 generation	*II-d LC50; Hardness - 5 Hardness = 50 mg/L	Hardness = 50 mg/L	*19-d LC 50; Hardness - 3 *10-d LC 50; Hardness - 5 *19-d LC 50; Hardness - 3	Eggs; Hardness - 10 mg/L Adult; Bardness - 10 mg/l • 30-d LC 50; Hardness - 3
(1/Su) u	%-hr LUSO Other*			8.1	88	18.2 0.0368	32.0	G2 61 G 5,243	12,0	26.2	16.0 16.0 G 11.9	20.2 19.0 17.0 0.771
Concentration (ng/L)	48.hr 96. LC50 LC	2,98	52.3	121 19		8		- G		- 26		223
ō	24-hr 4 1 C 50 1	21.2 0.12 9.64 75.8		10.2		21.8		,	62.6	32	1 1 1	28.1
	Type of Text	NNNNN	s	2.0	ш	vs. vs	s	li.	v v	5	NNN	v v r
	Species	Nass sp. Tubsfex tubsfex T. tubsfex T. tubsfex Tubsfective	Asellus aquaticus	Crangonyx pseudogracults Gammarus sp.	Orconectes virilis	Chironomus sp. Tanytarsus dissimilis	Acroneuria lyrorias	Clistoronia magnifica	Hydropsyche betten: Unidentified sp.	Unidentified sp.	Ephemerella grandis E. subvaria Pteronarcys californica	Amnicola sp. Amnicola sp. Physis gyrina
	Такон	Amelida, Oligochaeta	Crustacea, Isopoda	Crustacea, Amphipoda	Crustacea, Decapoda	Insecta, Diptera	Inecta, Peroptera	Insecta,	Fre respects	Insecta, Odonata	Insecta, Ephemeroptera	Mollusca, Gastropoda

F flow-through; S static; 2 G greater than; 3 NOTE, no observed-effect level;

		Type of	~	24-br 48-br 96-br	ehr 48.hr 96-hr			
	Species	Test		LC50 LC50	LC 50	Other.	Remarks	Reference
	Acroneuria pacifica	~		130	~	180	*72-hr LC 50	Jensen and Gaufin (1964a)
Plecoptera .	Pteronarcys californica	s			180	800	•72-hr LC50	Jensen and Gaufin (1964a)
	P. californica	S	30	8.0	67			Sanders and Cope (1968)

F : flow-through; S : static.

APPINDIX TAM F AZJ2; FOXICITY OF WATTRIOPNE # JHIC TO BENTHE MACROINGI RTERPATES

	Reference	Canton and Slooff (1977)	
	Remarks	•70-d EC 50 for overall reproductivity	
Concentration (ug/L)	Type of 24-br 48-br 98-br Test 1 C50 LC50 LC50 Other*	s . 1,200 . 65	Gattripeds
	Species	Mollos a. Lymnae's stagnalis	Gastropoda

F - flow-through; S static.

APPLINDIX TABLE A2.13: TOXICITY OF WATERBORNE 7-BHC TO BENTHIC MACROINVERTERRATES

						1		
		,	1 4	oncent	Concentration (ug/L)	(1)		
Taxon	Sancines	Lype of	74-5r 1C 50	LC 50	LC 50	Other.	Remarks	Reference
Platyhelminthes, Tricladia	Polycelis tenuis	CF		G ² 430 G 430	G 430			Green et al. (1986a)
Annelida, Oligochaetea	Limnodrilus hoffmeisteri L. hoffmeisteri/Tubilex tubilex	L.		G 4.30	3,150			Green et al. (1986b) Whitten and Goodnight (1966)
Crustacra, Isopoda	Asellus brevicaudus A. aquaticus	٠ <u>١</u>		10 G 430	37.5			Sanders (1972) Green et al. (1986b)
Crastacra, Amphipoda	Gammarus fasciatus G. fasciatus G. fasciatus G. puter G. puter G. puter G. puter G. puter G. puter	VVVV±VVVV	23.6	G 430 G 430 G 430 G 430	10 11 13,6 13,6 5,9		172h [C90 172h [C90	Sanders (1972) Sanders (1972) Harder et al. (1978) Sanders (1978) Gravert al. (1986) Rote (1986) Rote (1987) Stephenson (1983) Stephenson (1983)
Insecta, Diptera	Chironomus riparius C. riparius C. riparius C. riparius C. tentans	FAAAA		330	235 29.0 11.2 28.7		4th instar; pH = 4.0 4th instar; pH = 6.0 4th instar; pH = 8.0	Green et al. (1986b) Warwick Fisher (1983) Warwick Fisher (1983) Warwick Fisher (1983) Macek et al. (1976)
Insecta, Plecoptera	Pteronarcys californicus Leuctra mosofyi Protonemura meyeri	VEL 1	15	8.0 150 130	1, 30 1, 130			Sanders and Cope (1968) Green et al. (1986b) Green et al. (1984b)
Insecta, Trickoptera Insecta, Eplemeroptera Mofinca.	Hydropsyche angustipennis Raetis rhodani Caenis moesta Physa fontinalis	L L V L		G 430 330 185 54 10 1	3.0		LC 50 values are estimates	Macek et al. (1976) Green et al. (1986) Harper et al. (1977) Green et al. (1977)
Gastropoda					:			

			Č	Mr entr.	The work	Conventration (ig/L)		
		Type of 24-hr 48-hr 96-hr	24-hr	48.hr	36-hr			
Taxon Sp	Species	-	LC 50	0,01	05.27	Text LC50 1C50 LC50 Other*	Remarks	Reference
					i		The second secon	
Insecta, Pt	Peronarcys californica	v	170 55 15	۶	~			Sanders and Cope (196
Plecoptera								

F flow-through; S static.

APPENDIX TABLE A2.15: TOXICITY OF WALFPRORMEDING TO BENTHIC MACROINVERTEINPATES

				oncentr	3ii) uoite	Concentration (ug/L)		
Taxon	Species	Type of 24thr 48thr 96ths Text 10.50 LC50 LC50	29ahr 1 C 50	48.br LC 50	24-hr 48-hr 96-hi 1030 LC50 LC50 Other*	Other.	Remarks	Reference
Inecta, Plecoptera	Personarcys calderina S 1,000 1,100 300 .	~	3,000	3,000 1,100 380	38.0			Sanders and Cope (1968)
F - flow-through: S static.	e S statio							

		Peference	Stalling and Mayer (1972)	Stalling and Mayer (1972)	Stalling and Mayer (1972)	Staffing and Mayer (1972)	Stalling and Mayer (1972)	Karnak and Collins (1974)	Jensen and Gaufin (1964a)	Jensen and Gaufin (1%4b)	Sanders and Cripir (1968)	Sanders and Cope (1%8)	Jensen and Gaufin (196ks)	Jensen and Gaufin (1964b)	Sanders and Cope (1968)	Stalling and Mayer (1972)	
		Remarks		• 5-d LC50		• 5-d LC50	05 DT PTG .		• 72.hr LC 10	• 30-d LC 50			• 72-hr LC 50	* 30-d LC 50			
(1)		Other		9.0		1.0	53		320	7.2	,	,	2,450	392	,		
Concentration (ug/L)	46-hr	TC50 LC50 LC50	3,2	,	100	,	,		320	,	1,5	6.	1,800		2.0	*	
Concent	Type of 24-hr 48-hr 96-hr	17.20	٠						2,200		6.4	9,6	2,450		10		
	29-24			,	,			19.5	,		16	1.2	1	1	4		
	Type of	Test-	v	ш	S	v	la.	~	s	v	v	v	v	v	v	~	
		Species	Gammanus fasciatus	G, fasciatus	Orconer tes nais	Pilarmonetes kadiakensis	P. kadiakensis	Chironomus tentans	Acroneuria pacifica	A. pacifica	Claasonia sabidosa	Pteronarcella hadia	Pteronarcys californica	P. californica	P. californica	livecta, Odonata - Bobinira verticalis	
		Taxon	Crustama,	Amphipoda	Crustacea,	Decapoda		Insecta, Diptera	herta,	Plecoptera						Invecta, Odonata	

1 F - flow-through; S - static,

APPENDIX TANTE A2,12; TOXICITY OF WATTERORNE DIFFIDATE TO RENTHE MACROING REFERENTS

Taxon	Species	Type of Test ¹	Concentration (ug(1)) Type of 24-hr 98-hr 96-hr Test LC50 LC50 LC50 Other*	Concentration (ug/1) 20-hr / 8-hr 9-hr LC50 LC50 LC50 Other*	tron (ug/ 96-br	1)	Remarks	Reference
Insecta, Diptera	Incecta, Diptera — Chronomus tentans C. tentans	v ×	0.9			98.5	• 72-hr LC50	Karnak and Collins (1974) Hansen and Kawatski (1976)
hoorta, Plecoptera	Acronouria pacifica Claasvena sabulosa Preconarcella badia Preconarcys californica P, californica	~ ~ ~ ~ ~	55.5	42 24 4,5 2,3 0,58 3,5 1,5 1,5 1,5 1,5 1,5 1,5 1,5 1,5 1,5 1	24 0.58 0.5 10 0.5	55 . 29	• 72-br LC%0	Perrori and Gartín (1964) Sanders and Cope (1968) Sanders and Cope (1963) Perrori and Gadini (1964) Sanders and Gadini (1964)

 4 F - flow-through; S_{\odot} static, 2 G - greater than,

APPINDIX TABLE A2.18: TOXICITY OF WATERFORM FINDRIN TO MINTIR MACROINVERTERRATES

				Oncente	Concentration (ag/L)			
		Type of	24.hr	24.hr 48.hr 96.hr	96-hr			
Taxon	Species	Test	LC 50	LC10 LC50 LC50	LC 50	Other.	Remarks	Reference
Grustacea, Decapoda	Orconectes immunis	-			£			Thurston <u>et al.</u> (1985)
Insecta, Diptera	Tany tarsus dissimilis	i		0.83		,		Thurston et al. (1985)
Insecta,	Acroneuria pacifica	S			0,39	69.0	• 72-hr LC50	Jensen and Gaufin (1964a)
Plecoptera	Claassenia sabulosa	S	3,2	0.84	0,76			Sanders and Cope (1968)
	Pteronarcella badia	S	2,8	1.7	0.54			Sanders and Cope (1968)
	Pteronarcys californica	S	٠	7.8	2,4	3.7	* 72.hr LC50	Jensen and Gaufin (1964a)
	P. californica	s	0.4	960	0.25	,		Sanders and Cope (1968)
	P, dorsata	L			,	0.07	• 28-d LC50	Anderson and DeFoe (1980)
	P. dorsata	<u>.</u>			0,22	0,05	* 28-d EC50; behavioural EC50	Anderson and DeFoe (1980)
Insecta,	Prachycentrus americanus	L			0, 30	0.044	• 14-d LC50	Anderson and DeFoe (1980)
Tricoptera	B. americanus	_			0.23	0.017	 14-d EC50; behavioural EC50 	Anderson and DeFoe (1980)

 $^{^{1}}$ F = flow-through; S - static, 2 C, - greater than,

APPENDIX TAME A2.1%— FOXICITY OF WATERBARNE HEPTACHLOR TO BENTHE MACROINVERTERPARTS

Reference	Sanders and Cope (1968) Sanders and Cope (1968) Sanders and Cope (1968)
Remarks	
0ther*	
Type of 24-hr 48-hr 96-hr Teet ¹ LC 50 LC 50 LC 50	2.8
48-hr	9.0 6.4 6.0 4.0 8.0 5.6
24-hr	5 9 9
Type of Test ¹	~ ~ ~
on Spocies	Claasvenia sabulosa Pteronarcella badia Pteronarcys californica
Taxon	Invecta, Plecoptera

1 F = flow-through: S = static.

APPLINIX TABLE A2.29: TOXICHTY OF WATERFORMS MIREX TO BENTHIC MACPOINVEPTIUR ATES

				Concentration (ug/L)	atron (ug.	(1)		
	Species	Type of Test	24-hr 1-1-10	Type of 24-br 48-br 96-br Test I C 50 LC 50 LC 50	96-hr	ype of 24-hr 48-hr 96-hr Test LC30 LC30 LC50 Other	Prmarks	Reference
Crustacea. Amphipeda	Gammarus pw -1 timnaeus Hyallela azteca	F w		- G ² 1,000 -		1,32.4	• 126-4 WATC ⁴ • 25-4 LC50	Sanders et al. (1981) Naqvi and de la Cruz (1973)
Grustacea, Decapoda	Palaemonetes kadiakensis Procambarus blandingi P. hayi	N N N			0	6 - 1.0	• 120-hr LC50 • 95% mortality 5 diafter 194-hr exposure • 67% mortality 9 diafter 48-hr exposure	Naqvi and de la Cruz (1973) Ludke <u>et al.</u> (1971) Ludke <u>et al.</u> (1971)
Invecta, Diptera	Chironomus plumosus	Į.		G 1,000		G 34	• 30-d MATC	Sanders et al. (1981)
, Odonata	Invecta, Odonata Macromia sp.	V	,	1,000		,		Naqvi and de la Cruz (1973)

 $[\]Gamma$ - flow-through; S - static, 2 G - greater than, 4 L - less than, 6 MATC - maximum allowable poxecant concentration,

APPENDIX TABLE A2.21: TOXICITY OF WAFERFORM: IX'R TO BENTHIC MACROINVERTERRATES

			0	oncentr	Concentration (ug/L)	(1)		
Taxon	Species	Type of Text	24-hr LC 50	48-hr LC 50	96-hr 2.C 50	Other*	Remarks	Reference
								Man of the second
Crustacea,	Cammarus Tasciatus	_	,		2		Arocior 1242	Mayer et al. (1777)
Amphipeda	G. fasciatus	v	,	,	25	,	Aroclor 1248	Mayer et al. (1977)
	G. fasciatus	S			2,400		Aroctor 1254	Mayer et al. (1977)
	G. fasciatus	L			02	2.0	 10-d LC 50, Aroctor 1242 	Stalling and Mayer (1972)
	G. fasciatus	S		,	52		Aroclor 1248	Stalling and Mayer (1972)
	G. fasciatus	v			2,400	,	Aroclor 1259	Stalling and Mayer (1972)
	G. pseudolimpaeus	L.		,	73	8.7	* 30-d LC 50: Aroctor 1292	Nebeker and Puglisi (1974), Nebeker (1976)
	G. pseudolimnaeus	L	,	,	52	5.1	 30-d LC59, Aroclor 1248 	Nebeker and Puglisi (1974); Nebeker (1976)
	G. pseudolimnaeus	S			2.0		2,3.4" trichlorobiphenyl	Mayer et al. (1977)
	G. pseudolimnaeus	S			100	,	4,4' dichlorobiphenyl	Mayer et al. (1977)
	G. peradolimnaeus	v	,		120		2.4" dichlorobiphenyl	Mayer et al. (1977)
	G. pseudolimnaeus	S	,	,	150		2,4,6,2,4,6 hexachlorobiphenyl	Mayer et al. (1977)
	G. pseudolimnaeus	S	,		210		2,4,5,2,5 Pentachlorobyphenyl	Mayer et al. (1977)
		,				9	* 7 d 1 C 50. Armelor 1303	Stalline and Maser (1972)
Clustacea,	OLCOHOLICS HAIS	-				2	THE POST OF THE PARTY.	Commence and annual Commence
Decapoda	O. nais	S		,	,	00	 7-d LC 50; Aroctor 1259 	Stalling and Mayer (1972)
	O, nais	ů.	,		,	80	 7-d LC50, Aroclor 1259 	Stalling and Mayer (1972)
	O, nais	S			30	,	Aroclor 1242	Mayer et al. (1977)
	O, nais	S			100	,	Aroclor 1254	Mayer et al. (1977)
	Palaemoneres kadiakensis	i.	,		,	3.0	* 7-d LC 50: Arocilor 1259	Stalling and Mayer (1972)
	P. kadiakensis	L			3		Aroclor 1254	Mayer et al. (1977)
Insecta, Diptera	Tanytarsus dissimilis	L-	,	,		0.45	Lweek LC 50; Aroclor 1242	Nebeker and Puglisi (1974)
	T. dissimilie	ш			,	0.65	* 3-week LC 50; larvae: Aroctor 1248	Nebeker and Puelisi (1974)
	T, dissimilis	L-			,	0.45	. 3-week LC50; pupae; Aroclor 1248	Nebeker and Puglisi (1974)
Description Odenser	for house a constant in	L			000		Assertor 1242	Mayor of al. (1977)
may continue	School of the same	. 6			90		Accorded 1356	Manage of all (1922)
	i. verticalis	_ 0	,		007		4 - 4 - 1263	Continue of the continue (1979)
	i. verticalis	0	,	,	900		Arocior 1292	Statility and mayer (1972)
	L verticalis	,	,	,	700		Aracior 1.2%	Stalling and Mayer (1972)
	Macromia sp.	v.				800	 7-d LC 50; Anoctor 1242 	Stalling and Mayer (1972)
	Macromia sp.	v 1				1,000	• 7-d LC 50; Aractor 12%	Stalling and Mayer (1972)
	Macromia sp.	s			800		Aroclor 1292	Mayer et al. (1977)
	Macromia sp.	v			000	,	Aroclor 1254	Mayor et al. (1977)



	1,100	Tour			Phace	100	Phase Tech Tech	Spen	3	ē			5		ä	Sonore I'm	Transfer I	1		Spend	Senthir Committy	Ę		
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				Stage						(8/60)		_	(ug/L)					10.00		é				
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PPTDE	Safe 1	none.	Catostomus, commerson	∢ <	pas s	Z :	2 :	2 1	7 0	0.0552	; ;	- 0	P, C	- 0	ę c	0, 0	- 6	1,048		9 0	2 :		ei -	0.854.0
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PPTDE	San	none	Cottus.sp.	∢	3	. 25	2	2	16-6-	0.0562	7	0	0,	0	Ŷ	0	9 0	0.044		0				0,783.0
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		auou	Cyprinus.carpio	∢	3	2	2	P.	1 6- 6-	0.0869		0.	o.	o	o,	0		6.5	ī.	9			~\$ ·	2,877.0
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_	5	acou	lctalurus.nebulosus	4	Pag	2	2	2	1 6- 6-	0.068		o	o-	P	o,	0.	0	0.3%	m	0-	94 0-	-	á	4,353 B
	5	audu	Ictalurus. nebulosus	⋖	2ed	2	2	2	-6-6-	0.001	_	o-	o,	o-	o ₁	-0-	0	0.002		٥,	6	-	ci	2,000 p
×	-	augu	lctalurus.nebulosus	۷.	Sed	2 :	8	2	- 6- 6-	0.0066		9	0, 1	0	0 1	0	0	0.02	~ .	0 0	2 :		r. 6	7.121 0
2024		note	Ictalurus.nebulosus	۷.	pes :	2:	2	P	10-0-0	0.0037	0 0	9 0	e c	9 6	op o	0, 0	0 0	0.013		P 0	, ,		60	0.549 0
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100	safi	auou	ictaturus, nebulosus	∢	pes	4	e e	70	-6 -6 1	n.0869	179	o,	o.	O.	0-	-0-	0	0.054		o,	0		D.	0.621.0
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Penthuc Community	Diver.		•	0	2 0	170	170	17.0-	4N 0-	1 N 0	-0 NA	176 0-	AW 9-	AN 0- 1	TN 6"	4N 6-	4M 6-	1 0 ·	₩ 0-	200	4N 0-	5	4	2 :	W :	2 0	7	4N 0-	9	44.0	9	AN 9-	-0 NA	AM 9-		44 0-	AN 9-	44 6-	AN 0- 0	AN 0- 0	9 :	4N 0-	2 .		0	0	
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SIMPLE CORRELATIONS OF ORGANIC CONTAMINANT CONCENTRATIONS IN BENTHIC TISSUES AND SEDIMENTS - S. bairdi

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TABLE A4.2: COMPARISON OF PERFORMANCE OF MODIFIED McFARLAND-RUBINSTEIN MODELS 1 AND 2 IN PREDICTION OF BIO ACCUMULATION POTENTIAL FOR ORGANIC CONTAMINANTS -MIXED TAXA

		Model I			Model 2	
Sediment Para me te r	R^2	ь1	b ₂	R ²	ьI	b ₂
	0.25/*	0.231*	0.095	0.228	0.198*	0,10
Aldrin	0.256*	0.423*	0.095	0.228	0.198*	-0.04
a-BHC	0.425* 0.281*	0.423*	-0.036	0.504*	0.527*	-0.13
3-BHC y-BHC	0.161	0.058	0.146	0.153	0.029	0.14
z-chlordane	0.101	0.502*	0.023	0.686*	0.682*	0.14
y-chlordane	0.514*	0.526*	-0.061	0.707*	0.715*	-0.06
Dieldrin	0.315*	0.308*	0.020	0.307*	0.289*	0.06
DMDT	0.189	0.192	-0.010	0.302*	0.318*	-0.06
Endosulphan I	0.27.5*	0.274*	0.004	0.223	0.212	0.03
Endosulphan II	0.336*	0.341*	-0.022	0.330*	0.329*	0.00
Endosaipi kiri ir Endrin	0.147	0.123	0.060	0.108	0.070	0.07
Endosulphan sulphate	0.331*	0.157	0.279*	0.314*	0.108	0.28
Heptachlor epoxide	0.222	0.246	-0.052	0.252	0.279*	-0.06
Heptachlor	0.329*	0.336*	-0.029	0.618*	0.654*	-0.16
Mirex	0.362*	0.361*	0.001	0.585*	0.614*	-0.11
Oxy-chlordane	0.315*	0.315*	0.000	0.286*	0.283*	0.00
PCB	0.583*	0.595*	-0.076	0.577*	0.580*	-0.02
p,p-DDD	0.427*	0.431*	-0.018	0.585*	0.584*	-0.00
p,p-DDE	0.374*	0.386*	-0.031	0.355*	0.339*	0.05
p,p-DDT	0.251	0.253*	-0.006	0.420*	0.450*	-0.10
HCB	0.508*	0.085	0.429	0.518*	-0.133	0.58

^{*} Indicates significance (p < 0.05) of model (R 2) based on F-test or standard partial regression coefficient (b) based on t-test.

See text page 3.6 for definition of model terms. TOC was not significantly correlated with SE or $P_{\rm c}$,

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APPENDIX 5

Examples and Computational Details

APPENDIX 5: EXAMPLES AND COMPUTATIONAL DETAILS

Sediment Background Approach

The following examples of sediment background concentration ranges, the upper limits of which could be used as sediment quality objectives, are taken from Mudroch et al. (1986):

Type of Sampling Area	Bulk Copper (ug/g dry weight) in Lake Ontario Sediments
Depositional Basins:	
o surface	26-109
o background (cores)	35-56
Nondepositional Zones:	
o surface	2,1-200
o background	60-100
Embayments:	
o surface	3-265
o background	-
Harbours:	
o surface	1.0-860
o background	-
River Mouth:	
o surface	6.8-83
o background	-

The choice of appropriate types of background data on which to base sediment quality objectives is a value judgement relating to the intent of the objectives.

Sediment-Water Equilibrium Partitioning Approach

The estimation of interstitial water concentrations from sediment concentrations involves the assumption that the distribution of a contaminant between sediment and interstitial water phases is governed by rapid and continuous exchange between these two phases. This assumption of thermodynamic equilibrium at the sediment-water interface

implies that the sediment phase/aqueous phase concentration ratio is a constant for a given sediment. The distribution can be represented as:

$$K_D = \frac{C_s}{C_{iw}}$$

where: K_D = the thermodynamic sediment-water partition coefficient for a specific contaminant.

 $C_{\rm S}$ = sediment concentration of the specific contaminant (dry weight), and $C_{\rm iw}$ = interstitial water concentration of the specific contaminant.

Laboratory sorption experiments have demonstrated that $K_{\rm D}$ values of nonpolar, nonionic organic contaminants are significantly correlated with sedimentary organic carbon content. Because organic matter is apparently the sedimentary fraction that mediates sediment-water distributions, sedimentary concentrations of nonpolar organic contaminants are normalized to organic carbon content for the equilibrium partitioning approach. That is:

$$K_{oc} = \frac{C_s}{C_{iw}} \times \frac{1}{f_{oc}} = \frac{K_D}{f_{oc}}$$

where: $K_{oC} = \text{organic}$ carbon-normalized partition coefficient for a specific contaminant, and

 f_{OC} = fraction (on a weight/weight basis, in decimal form) of organic carbon in the sediment (dry weight).

If a K_{OC} value and a water quality criterion $(C_{\rm w/cr})$ for a specific contaminant are known, an organic carbon-normalized sediment quality value $(C_{\rm s/cr})$ can be determined as:

$$C_{s/cr} = K_{oc} \times C_{w/cr}$$

Because K_{QC} values are not available in published literature for all contaminants, more widely available octanol-water partition coefficients (K_{QW} values) are used to estimate

 $K_{\rm oc}$ values. Several laboratory studies have demonstrated that $K_{\rm ow}$ and $K_{\rm oc}$ values for a given nonpolar organic contaminant are highly correlated. This relationship is expressed in the form:

where: a and b are empirically derived constants.

This correlation implies that the partitioning of a nonpolar organic contaminant between water and an immiscible organic solvent (octanol) is mechanistically analogous to its distribution between water and sedimentary organic matter.

Sediment-Biota Equilibrium Partitioning Approach

In the sediment-biota equilibrium partitioning approach, the expression used to establish sediment quality values is based on:

$$BCF_{B-S} = C_B/C_{s/\infty}$$

where: BCF_{B-S} = bioconcentration factor (partition coefficient) of a specific contaminant between sediment and biota,

C_B = contaminant concentration in biota (normalized to lipid content),

 contaminant concentration in sediment (normalized to organic carbon content).

This expression can be converted to:

$$log(C_{S/OC}) = log(C_B) - log(BCF_{B-S})$$

An approximation of BCF $_{B-S}$ was established by McFarland (1984) based on a very limited amount of data. Log(BCF $_{B-S}$) was given a constant value of -0.28. Thus, if a body burden limit is available for a given contaminant, the appropriate sediment quality value can be derived from:

$$log(C_{s/cr}) = log(C_{B/cr}) + 0.28$$

where: $(C_{S/Cr})$ = sediment quality value for a specific contaminant, and $(C_{B/Cr})$ = body burden limit for the contaminant (lipid normalized).

If BCF_{B-S} is not given a constant value, an empirically derived value for sediment organic matter/lipid partitioning would have to be established for all relevant contaminants and benthic species. This would require a considerable amount of bioaccumulation research.

The body burden limit generally originates from human health considerations and may not be applicable to benthic organisms. However, the acceptable limit for human foods, such as fish, can be converted to an acceptable limit for benthic organisms by application of a food chain biomagnification factor (BMF). For example, DDT biomagnifies through the food chain approximately ten times (BMF = 10) from benthos to fish (Borgmann and Whittle, 1983).

Biota-Water Equilibrium Partitioning

Because body burden limits have been established for few contaminants, a method has been devised to calculate tissue body burden limits from water quality criteria. The operative assumption for this method is that equilibrium body burdens of organisms will be acceptable in interstitial water with contaminant concentrations in compliance with water quality criteria. The calculation is based on the expression:

$$BCF_{B-W} = C_B/C_W$$
 or $log(C_B) = log(BCF_{B-W}) + log(C_{W/CT})$

where: (C_B) = lipid-normalized body burden of the specific contaminant, (BCF_{R-W}) = bioconcentration factor (partition coefficient) of the contaminant

between biota and water, and

(Cw/cr) = water quality criterion for the contaminant.

Then:
$$C_{s/cr} = C_{w/cr} \times K_{\infty}$$

 $\mathsf{BCF}_{\mathsf{B-W}}$ is often estimated by K_{OW} , as strong linear log-log correlations between $\mathsf{BCF}_{\mathsf{B-W}}$ and K_{OW} have been reported for some compounds in fish.

Water Quality Criteria

This approach is similar to the sediment-water partitioning approach, except that an empirical site-specific relationship between interstitial water and sediment concentrations would be used (instead of a generic $K_{\rm OC}$) to derive a sediment quality objective from the water quality objective. Depending on the form of this relationship, the sediment criterion concentration could be expressed either on a bulk sediment or organic carbon-normalized basis.

Screening Level Criterion

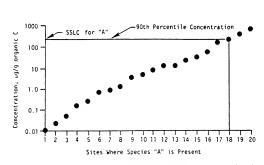
An example of the SLC approach is illustrated in Figure A5.1 (Neff et al., 1986). The calculation of species screening level concentration (SSLC, shown in a) is repeated for a large number of species, then the general SLC calculated (as shown in b). Each point on each graph represents a sampling site. Each site has several SSLCs for each species, and a single SLC.

Apparent Effect Threshold

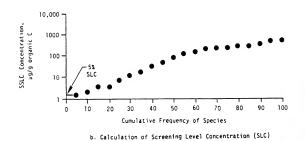
An example of the AET approach is shown in Figure A5.2 (Tetra Tech, 1986). All sampling sites with contaminant concentrations above the AET show benthic depression and/or sediment toxicity. All sites with concentrations below the potential effect threshold (PET) show neither depression nor toxicity. The PET is a conservative criterion, while the AET is less stringent but more defensible in specific cases.

Bioassay Approaches

The principle of the bioassay approach, whether field or laboratory data are used, is illustrated in Figure A5.3 (Finney, 1971). Each point on the graph is a sample, characterized by a percent response (percent mortality, percent of maximum density, etc.). The percentages follow a sigmoid curve, and are therefore transformed to probits for linear curve fitting. The concentration corresponding to the 50% response is the LC50.



a. Calculation of Species Screening Level Concentration (SSLC)



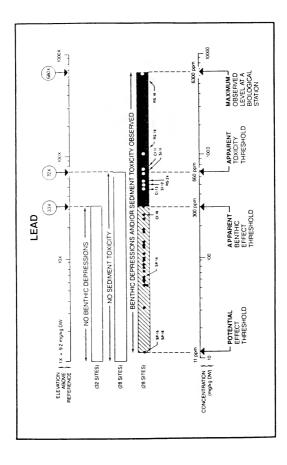
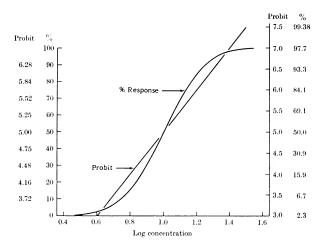


FIGURE A5.3: PRINCIPLE OF BIOASSAY APPROACH



Examples Using the Sediment Toxicity Database

Copper was used as an example to illustrate application of the Appendix I data to development of sediment quality criteria. Several approaches are possible. Since a water quality criterion exists, the Sediment-Water Partitioning approach is feasible. The AET approach is also illustrated. These approaches are compared to the Background approach based on background data from Mudroch et al. (1986).

Sediment-Water Partitioning

The MOE water quality objective for protection of aquatic life is 5 ug/L. A sediment-water distribution coefficient of 3.89 L/g was estimated from the geometric mean ratio of corresponding sediment and water concentrations. Published coefficients could also be used. Thus, the sediment quality criterion would be:

SQC =
$$5 \underline{ug}$$
 · $3.89 \underline{L}$ = $19.45 ug/g$ (say 20 ug/g)

Apparent Effects Threshold (AET)

The lowest copper concentration in the toxicity database above which \underline{all} sediment samples produced a significant response was 96 ug/g. At lower concentrations, some, but not all, samples produced a significant response. Thus, the sediment quality criterion would be:

$$SOC = 96 \, \text{ug/g}$$

The highest concentration below which no samples produced a significant response was 3 ug/g. This would be the potential effect threshold.

Significance in this example was not a statistical criterion since most authors did not determine statistical significance. Arbitrarily, a survival of less than 50% was considered a significant response. Control sample survival, when reported, was always much better than this.

Background Concentration

Background copper concentrations in sediments were reported by Mudroch et al. (1986), for depositional and non-depositional areas. The maximum of these two concentrations was 100 ug/g. Thus, the sediment quality criterion would be:

$$SQC = 100 \text{ ug/g}$$

This criterion agrees closely with the AET criterion of 96 ug/g.

Other Approaches

Sediment-Biota and Water-Biota Partitioning approaches were not used for copper since tissue concentration criteria do not exist.

The SLC approach would be feasible only if densities of individual benthic species were involved in the database. At present, only total organism densities are included.

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5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In summary, the following conclusions can be made.

- Nine different approaches to calculation of sediment quality objectives have been described in the literature, each with different input data requirements. These include an approach based on sediment 'background' concentrations, approaches based on sediment-water-biota partitioning coefficients applied to existing water or tissue objectives, approaches based on sediment contaminant concentration-biological response relationships from field studies, and an approach based on concentration-response relationships from laboratory (single contaminant) studies.
- 2. The MOE In-Place Pollutants Program database is primarily of use in generating pertinent partitioning coefficients or concentration response relationships in the field. The data for most organic contaminants suggest benthic tissue-sediment concentration relationships following the McFarland-Rubinstein model. However, the data for most metals do not indicate good correlations between concentrations in benthic tissues and sediment fractions.
- 3. The data required for application of sediment background and field concentration-response approaches are currently available for most contaminants addressed in this study, although it has not been determined from the database whether concentration-response relationships exist. Partitioning coefficients or bioassay response data will have to be generated for some contaminants in order to apply other approaches.

5.2 Recommendations

On the basis of these conclusions, the following recommendations have been developed.

 Since sources of outstanding concentration-response data often contain information on numerous contaminants, it will be most efficient for a single contractor to undertake development of numerical criteria for all contaminants addressed in this study. This will also ensure consistency of approach and, therefore, increase the defensibility of the resulting sediment quality objectives.

- It is essential, as a first step in generating sediment quality objectives, to define the intent of those objectives, in terms of taxa to be protected and adverse effects to be prevented. These value judgements determine the choice of appropriate coefficients and other input data which will be utilized in deriving sediment contaminant objectives. In effect, these judgements amount to a toxicity objective, and should be endorsed by the regulatory agency.
- A priorization of approaches will be required in the event that different approaches to derivation of objectives result in different numerical criteria.
 This strategy should be defined a priori and endorsed by the regulatory agency.
- 4. An iterative process of criteria development is recommended, in which interim criteria would be issued based on best available information, subject to review as data gaps are filled, and finalization only when additional data appear to have little effect on the resulting criterion.

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